APPLICATION OF TRIANIONIC PINCER LIGANDS TO REACTIONS INVOLVING GROUP VI ALKYLIDYNES, METAL-METAL MULTIPLE BONDS, AND GROUP IV AMIDES

By

ANDREW J PELOQUIN

A THESIS PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

UNIVERSITY OF FLORIDA

2008

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
01 AUG 2008	**N/A**	**-**

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Application Of Trianionic Pincer Ligands To Reactions Involving Group VI Alkylidynes, Metal-Metal Multiple Bonds, And Group IV Amides	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **University Of Florida**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) **AFIT/ENEL**	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S) **Cl09-0020**

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release, distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**	**UU**	**162**	

The views expressed in this thesis are those of the author and do not reflect the official policy or position of the United States Air Force, Department of Defense, or the U.S. Government.

ACKNOWLEDGMENTS

As this project draws to a close, I am extremely grateful to many individuals who have made this achievement possible.

I would like to first thank my advisor, Dr Adam Veige. His patience has made this research possible, given the numerous constraints my situation provided. I would also like to thank all the members of the Veige group for making my transition into his lab fairly effortless. Recognition must also be given to Khalil Abboud, who provided invaluable data through X-ray diffraction studies. I also thank the other members of my committee, Dr Stephen Miller and Dr Michael Scott for their time in reviewing my research.

Many faculty of the Department of Chemistry at the United States Air Force Academy also deserve much thanks for molding me into the scientist I am today, most importantly, my undergraduate advisor, Dr Gary Balaich, whose love for pure science has continued to motivate me throughout my educational endeavors. Without the extensive practical laboratory experience he provided, I would have been unable to complete this thesis in such a short period of time. Lastly, I would like to thank Lt Col (Ret) Ronald Furstenau; it was his passion for education which inspired my love of learning, now and for future quests.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Abstract of Thesis Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Master of Science

APPLICATION OF TRIANIONIC PINCER LIGANDS TO REACTIONS INVOLVING GROUP VI ALKYLIDYNES, METAL-METAL MULTIPLE BONDS, AND GROUP IV AMIDES

By

Andrew J Peloquin

August 2008

Chair: Adam S Veige
Major: Chemistry

In an effort to isolate a pincer-support tungsten alkylidyne, several new tungsten alkylidenes and a ditungsten compound have been isolated, supported by the previously reported OCO^{3-} pincer ligand [3,3"-di-*tert*-butyl-2,2"-di-(hydroxy-κO)-1,1':3',1"-terphenyl-2'-yl-$\kappa C^{2'}$] (^{t}BuOCO **1**). When the ^{t}BuOCO ligand precursor is treated with $W(OAr)_2(CH_2(CH_3)_3)$-$(\equiv C(CH_3)_3)$ (OAr= 2,6-diisopropylphenoxide) in benzene, the alkylidene complex [^{t}BuOCO]-$W(=CH(CH_3)_3)(O\text{-}2,6\text{-}^i Pr_2\text{-}C_6H_3)$ (**3**) results and was characterized by a combination of one and two dimensional NMR spectroscopy, single-crystal X-ray crystallography, and combustion analysis. To aid in the final α abstraction, $W(CH_2(CH_3)_3)_3(\equiv C(CH_3)_3)$ was next combined with **1**, but the reaction resulted in a complicated mixture of products. From this mixture, two closely related structural isomers of the form {[^{t}BuOCO]$(CH_3)_3$CCH=}W(μ-^{t}BuOCHO)W-{=CHC$(CH_3)_3$[^{t}BuOCO]} (**4** and **5**) were isolated. This bridged, dinuclear complex was analyzed by single-crystal X-ray crystallography. Finally, the reaction of $(NMe_2)_3W\equiv W(NMe_2)_3$ with two equivalents of **1** results first in [^{t}BuOCHO]$(NMe_2)W\equiv W(NMe_2)$[^{t}BuOCHO] (**7**) and after prolonged heating, [^{t}BuOCHO]W$(\mu\text{-}NMe_2)_2(\mu\text{-}O)$W[^{t}BuOCHO] (**8**). These complexes were analyzed by a combination of NMR spectroscopy, single-crystal X-ray crystallography, and

combustion analysis. The exact mechanism of formation for **8** is not yet know, but it potentially represents a rare example of the oxidative addition of water to an early transition metal.

CHAPTER 1
INTRODUCTION

Interest in high oxidation state alkylidene and alkylidyne complexes for application to alkene and alkyne metathesis has grown steadily since the discovery of metal-carbon multiple bonds approximately thirty years ago.[1,2,3,4] Alkylidyne species have received comparatively less attention than their alkylidene analogues, despite their application to nitrile-alkyne cross metathesis (NACM). NACM has the potential to become increasingly important as it represents a method to prepare novel alkynes from relatively accessible nitriles.[5,6]

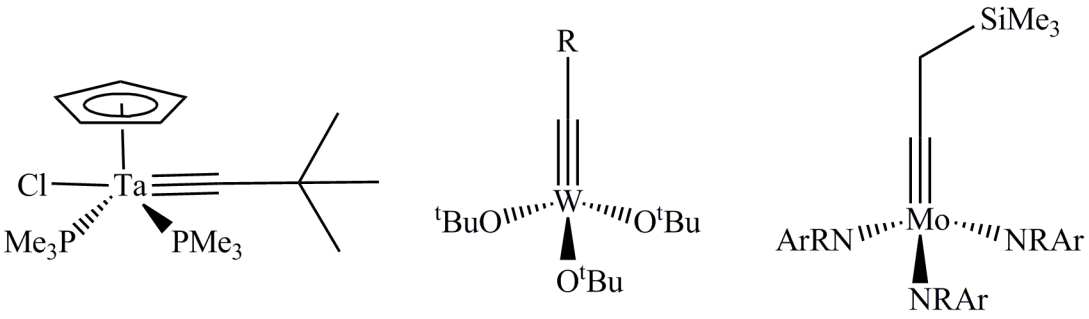


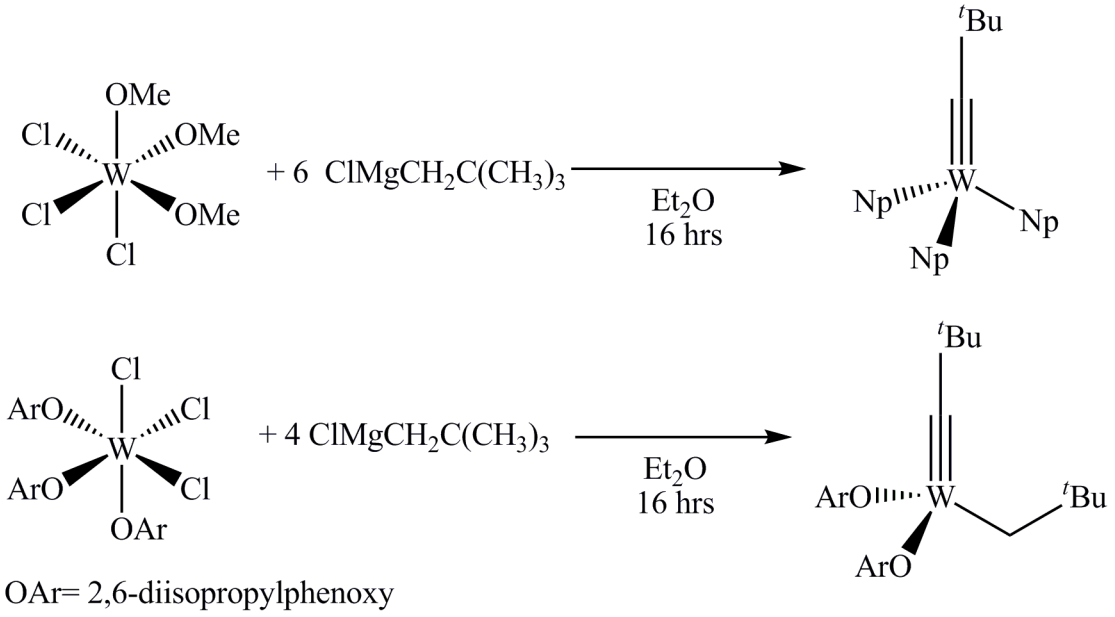
Figure 1-1: Examples of high-oxidation state metal-alkylidynes

A metal alkylidyne contains a metal-carbon triple bond. The research described herein focuses on Schrock-type alkylidynes, which are alkylidyne complexes in which the metal is in its highest oxidation state. These types of compounds were first prepared from tantalum[7], but are now commonly prepared from tungsten[8] and molybdenum[9] and, to a lesser extent, chromium[10] and rhenium (Figure 1-1).[11] In high-oxidation state alkylidynes, the alkylidyne carbon participates considerably in π-donation to the metal center and is considered a 6-electron donor. Despite such extensive π-donation, most high-oxidation state alkylidynes are electron deficient. The complex is stabilized by π-donation from the remaining ligands.

Schrock-type alkylidynes are generally formed by one of four methods, the most common being deprotonation of an α-CH or by α-elimination. Rarely, these complexes can be

formed by metathesis of an alkyne across a metal-metal triple bond, or by a reductive recycle strategy.

α-abstraction and α-elimination represent the most commonly encountered methods for the synthesis of most high-oxidation state alkylidynes. In α-elimination method, the α-C-H bond oxidatively adds to the metal, forming an alkylidyne from an alkylidene. More common in recent systems is α-abstraction. In Figure 1-2, the Grignard reagent acts as a base, deprotonating the α-carbon, forming an alkylidene from an alkyl and an alkylidyne from the alkylidene.[12,13] The exact order in which the alkylation and abstraction steps occur in these systems is not currently known.



OAr= 2,6-diisopropylphenoxy

Figure 1-2: Two examples of α-abstraction to produce tungsten-alkylidynes

The third, and one of the less frequently encountered methods for alkylidyne formation, is metathesis involving a W≡W moiety. [14] The scission of ditungsten hexa-*tert*-butoxide ((^{t}BuO)$_3$W≡W(O^{t}Bu)$_3$) (**I**) by an alkyne yields an alkylidyne of the form (^{t}BuO)$_3$W≡CR (**II**) (Figure 1-3). The R group is determined by the nature of the alkyne used in the reaction.

The fourth and final way in which high-oxidation state alkylidynes are generated is by a reductive recycle strategy (Figure 1-4). Fürstner reported the reaction of Mo[N(^{t}Bu)Ar]$_3$ (**III**) with CH_2Cl_2, which afforded a mixture of the chloride (**IV**) and the methylidyne species (**V**).[15] Kraft added magnesium to the system.[16] Magnesium present in the reaction mixture reduced the chloride species back to the starting material which could then re-enter the reaction. The result was a one-pot synthesis of a molybdenum alkylidyne from a terminal dichloride.

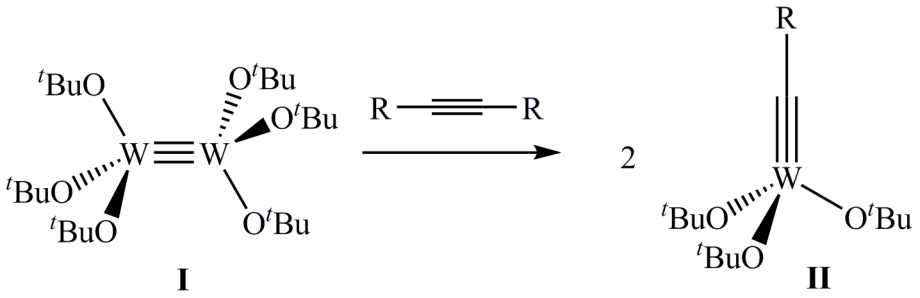


Figure 1-3: Metathesis cleavage of W≡W to form alkylidyne

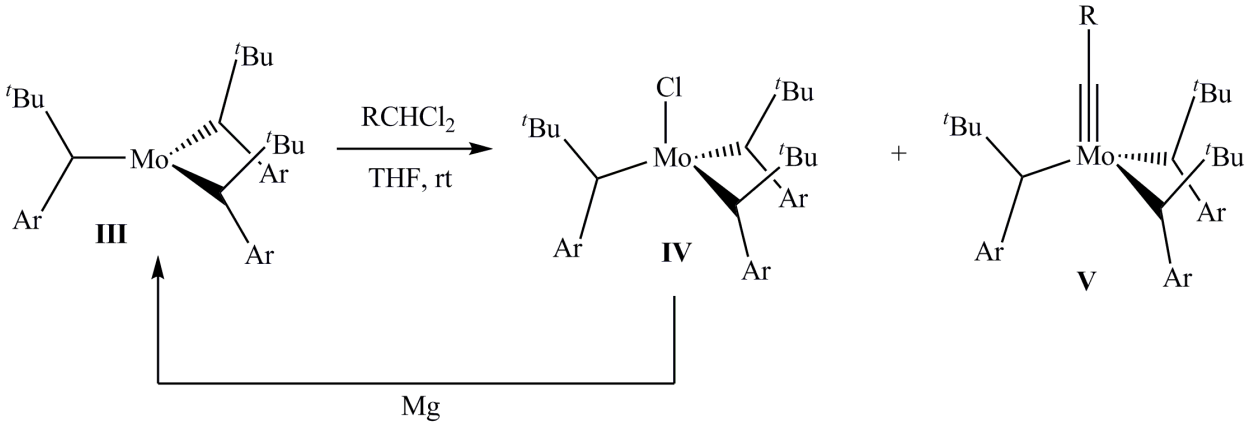


Figure 1-4: Reductive recycle strategy for alkylidyne synthesis

The primary goal of this research is to generate a highly reactive tungsten alkylidyne catalyst for NACM. NACM involves the conversion of a metal-carbon triple bond (alkylidyne) to a metal-nitrogen triple bond (nitride), or vice versa (Figure 1-5). A metal-alkylidyne can undergo a [2+2] cycloaddition with a nitrile to produce an azametallacyclobutadiene intermediate. This anti-aromatic intermediate can then undergo retro-cycloaddition to yield the

desired alkyne and a metal-nitride. A sacrificial alkyne is then employed to convert the metal-nitride back to a metal-alkylidyne to continue the catalytic cycle. A major roadblock to the catalytic version of the reaction is the high-energy azametallacyclobutadiene intermediate, which effectively makes either the alkylidyne or nitride a thermodynamic sink.

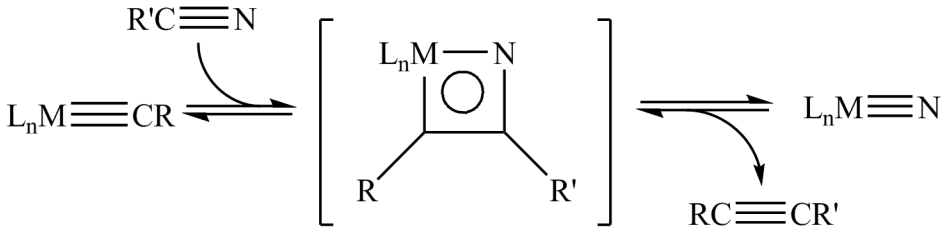


Figure 1-5: Mechanism of nitrile-alkyne cross metathesis (NACM)

In 2007, the first catalytic example of NACM was reported by Johnson et al.[17] A tungsten-nitride of the form $(RO)_3W{\equiv}N$ was found to reversibly convert to the corresponding ethylidyne upon treatment with 3-hexyne. In the presence of *p*-methoxyaniline, the corresponding alkyne was formed. Unfortunately, the system was rather sluggish and was limited in substrate scope.

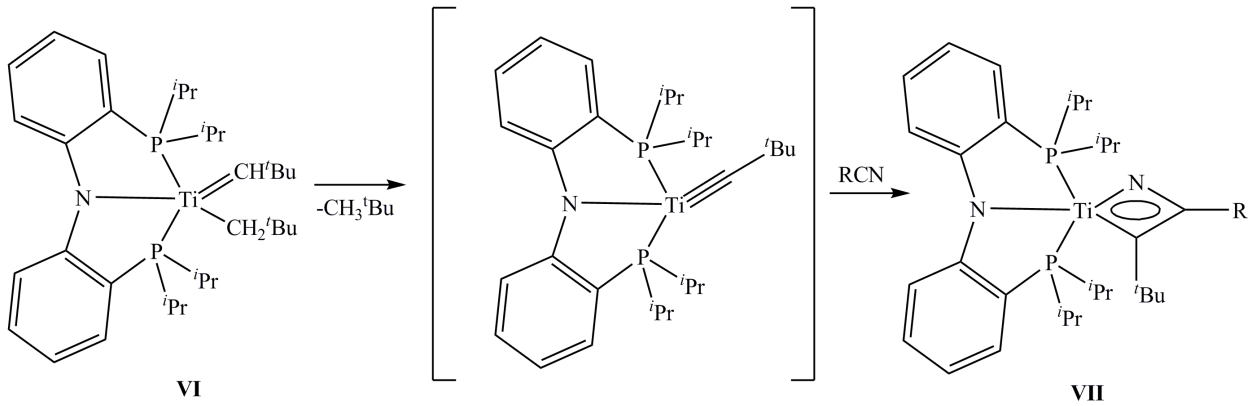


Figure 1-6: Pincer-type ligand supported alkylidyne

In 2005, the novel titanium alkylidene-alkyl complex (PNP)Ti=CH^{t}Bu(CH$_2$^{t}Bu) (**VI**) was reported by Mindiola et al. (Figure 1-6).[18] This complex features a tridentate, pincer-type ligand. In 2007, the same group found the complex to react with bulky nitriles to provide the first isolated azametallacyclobutadiene (**VII**). This complex showed promise for NACM but,

unfortunately, required an external electrophile, namely $ClSi(CH_3)_3$ or $AlMe_3$, to liberate the alkyne.

The following research aims to marry the ideas of Johnson and Mindiola. A high-oxidation state, group VI alkylidyne will be used, as these have been shown to successfully complete the NACM cycle. The extreme reactivity of a highly strained, pincer-type geometry will also be exploited. By using these two approaches in the same system, the resulting complex should be highly reactive and successfully complete the NACM cycle. The trianionic pincer ligands designed previously by the Veige group, in particular, the previously reported OCO pincer ligand [3,3"-di-*tert*-butyl-2,2"-di-(hydroxy-κO)-1,1':3',1"-terphenyl-2'-yl-$\kappa C^{2'}$] (^{t}BuOCO **1**), are ideal for use in an NACM system (Figure 1-7).[20]

There are three major reasons why these ligands are well-suited for application to a NACM catalyst. First, the trianionic nature of the pincer ligand allows access to the +6 oxidation state required for the alkylidyne. Second, the rigid planarity of the ligand backbone imposes geometry restraints around the metal center which should help increase its reactivity. Finally, the strong M-C bond present should distort the alkylidyne out of the plane of the ligand, further increasing the reactivity of the resulting complex.

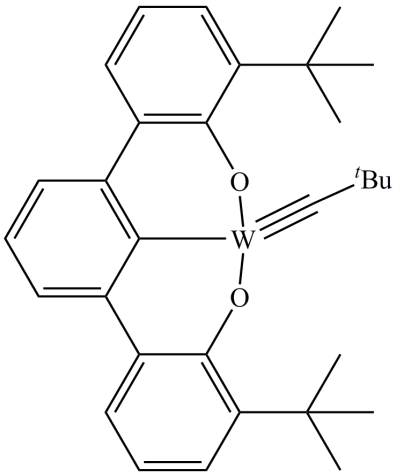


Figure 1-7: Target molecule

CHAPTER 2
PROGRESS TOWARDS A TUNGSTEN ALKYLIDYNE SUPPORTED WITH A TRIANIONC OCO^{3-} PINCER LIGAND

Synthesis and Characterization of [^{t}BuOCO]W(=CHC(CH$_3$)$_3$)(O-2,6-^{i}Pr$_2$-C$_6$H$_3$) (3)

The ^{t}BuOCO ligand precursor (**1**) was treated with one equivalent of W(OAr)$_2$-(CH$_2$C(CH$_3$)$_3$)(≡CC(CH$_3$)$_3$) (OAr = 2,6-diisopropylphenoxide) (**2**) in hot (85 °C) benzene for two hours, resulting in formation of a deep red solution of [^{t}BuOCO]W(=CHC(CH$_3$)$_3$)(O-2,6-^{i}Pr$_2$-C$_6$H$_3$) (**3**) (Figure 2-1). The molecular structure of **3** was confirmed by a combination of single-crystal X-ray crystallography and one- and two-dimensional NMR techniques. The complex features the tridentate, trianionic pincer ligand as part of the distorted square-pyramidal geometry around the tungsten center.

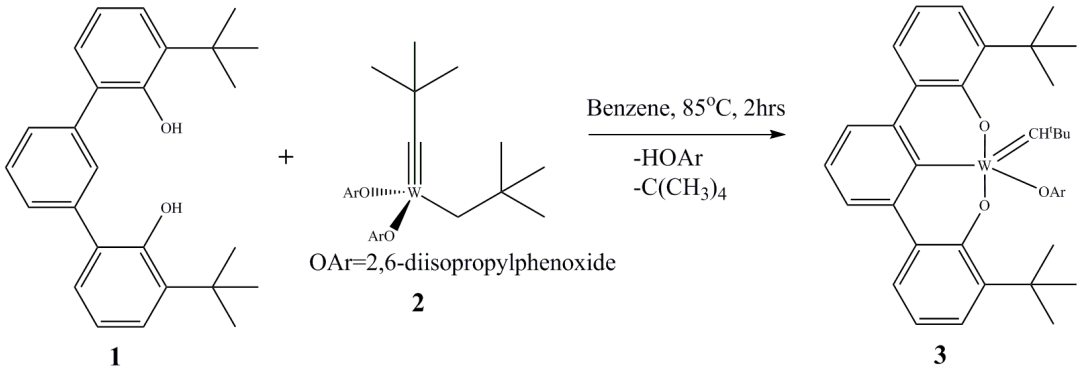


Figure 2-1: Synthesis of [^{t}BuOCO]W(=CHC(CH$_3$)$_3$)(O-2,6-^{i}Pr$_2$-C$_6$H$_3$) (**3**)

The coordination sphere is completed by 2,6-diisopropylphenoxide and a neopentylidene moiety. The 2,6-diisopropylphenol formed during the reaction proved difficult to remove, so all NMR data is of solutions containing one equivalent of free phenol. The *t*-butyl groups of the ligand resonate at 1.44 ppm in the ^{1}H NMR spectrum, their equivalence indicative of overall C_s symmetry. The 2,6-diisopropylphenoxide is oriented such that the two isopropyl groups are diastereotopic. The methine protons of the isopropyl groups resonate at 4.09 ppm and 2.39 ppm, and the methyl protons resonate at 1.42 ppm and 0.69 ppm. A singlet, attributed to the

alkylidene proton, is observed at 5.54 ppm. The identity of this peak was confirmed by HMQC NMR. The cross-peak correlated with the signal at 5.54 ppm in the ^{1}H NMR also correlated with the resonance at 272.2 ppm in the $^{13}C\{^{1}H\}$ spectrum, associated with the alkylidene carbon.

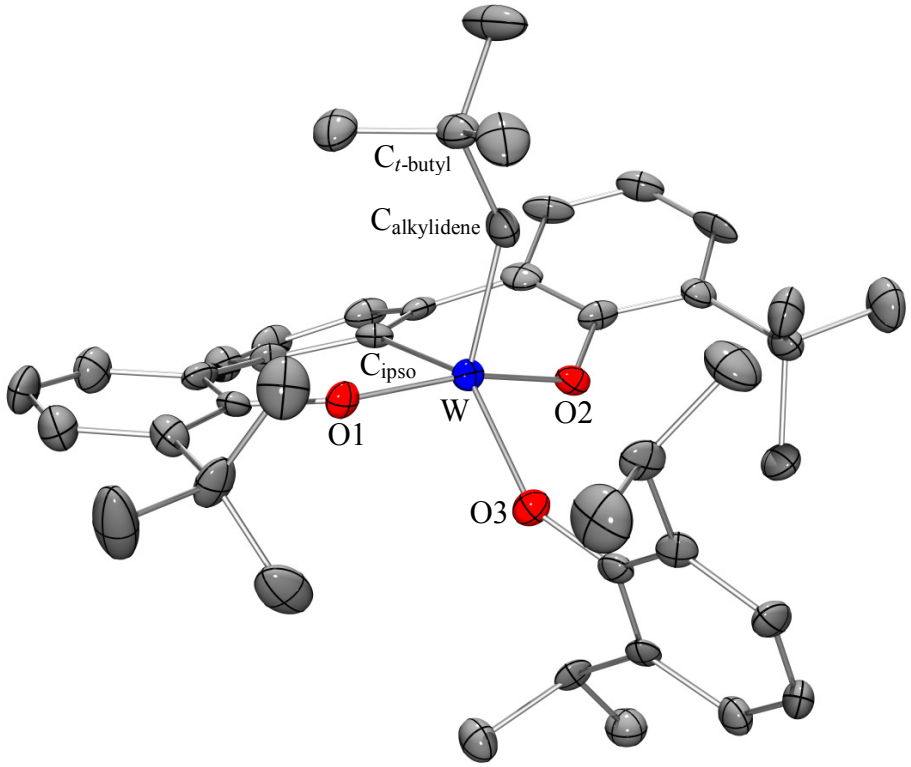


Figure 2-2: Molecular structure of **3**. Ellipsoids shown at 30% probability level; hydrogen atoms are omitted for clarity. Only one molecule of the asymmetric unit is shown.

A single crystal was obtained by slow evaporation of a diethyl ether solution and analyzed to confirm the structure of **3** (Figure 2-2). The molecule possesses C_1 symmetry in the solid state. The *t*-butyl of the neopentylidene moiety rests above an oxygen atom of the pincer ligand, with a $C_{t\text{-butyl}}$-$C_{alkylidene}$-W-O1 torsion angle of only 3.6(9)°. The alkylidene moiety occupies the apical position, with the ^{t}BuOCO ligand and the 2,6-diisopropylphenoxide occupying the basal positions. The positioning of the mirror plane in the C_{ipso}-W-$C_{alkylidene}$ plane can be seen by comparing the two molecules of the asymmetric unit (Figure 2-3). The two conformations must interconvert readily in solution, with free rotation around the W-$C_{alkylidene}$

bond. The 2,6-diisopropylphenoxide is positioned with one isopropyl group above the basal plane and one below the plane. This supports the nonequivalence of the isopropyl groups in the ^{1}H NMR spectrum. The W-$C_{alkylidene}$ distance of 1.917(8) Å and the W-$C_{alkylidene}$-C angle of 139.9(7)° are not atypical.[21,22,23,24] The ligand backbone is slightly twisted to relieve steric congestion, with the rings of the ligands arms rotated 22.74(10)° with respect to each other, which is also not unusual for this ligand system.[20]

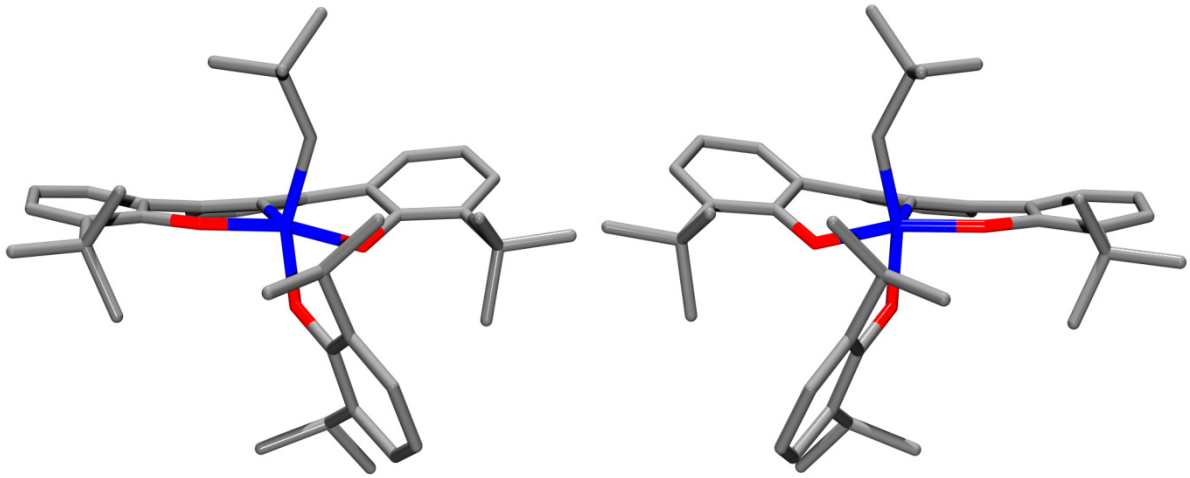


Figure 2-3: Two molecules of asymmetric unit of **3** demonstrating mirror symmetry

There are two possible routes by which **1** could form. In one method, the first step in the reaction is addition of the –OH group from **1** across the triple bond of the alkylidyne in **2**. The reaction proceeds by alcoholysis of the remaining hydroxyl group of **1** by one 2,6-diisopropylphenoxide, and C-H activation and alkyl elimination of neopentane to bind the backbone of the ligand to the tungsten center. This would leave one 2,6-diisopropylphenoxide bound the tungsten atom as seen in **3**. Another possibility is for alcoholysis and C-H activation to bind all three donor sites of the ligand to the tungsten atom. The alkylidyne is left intact, but then one equivalent of the 2,6-diisopropylphenol formed adds across the tungsten-carbon triple bond, leaving the alkylidene and phenoxide as observed.

Synthesis and Characterization of {[^{t}BuOCO](CH$_3$)$_3$CCH=}W(μ-^{t}BuOCHO)-W{=CHC(CH$_3$)$_3$[^{t}BuOCO]} (4 and 5)

Addition of 2,6-diisopropylphenol across the alkylidyne bond is a possible route for formation of **3**; thus, W(CH$_2$C(CH$_3$)$_3$)$_3$(≡CC(CH$_3$)$_3$) was next chosen as an alkylidyne source. The neopentane formed during the reaction should be unreactive and so the resulting complex should retain the alkylidyne moiety. The reaction between ^{t}BuOCO and W(CH$_2$C(CH$_3$)$_3$)$_3$-(≡CC(CH$_3$)$_3$) in benzene required prolonged heating (72 hours) at extremely elevated temperatures (145°C) to obtain appreciable conversion to {[^{t}BuOCO](CH$_3$)$_3$CCH=}W(μ-^{t}BuOCHO)W{=CHC(CH$_3$)$_3$-[^{t}BuOCO]} (**4** and **5**) (Figure 2-4). Single-crystal X-ray crystallography was used to elucidate the structures of **4** and **5**, related structural isomers present in the product mixture. Both compounds consist of two distorted square-pyramidal tungsten centers bridged by one ^{t}BuOCHO ligand.

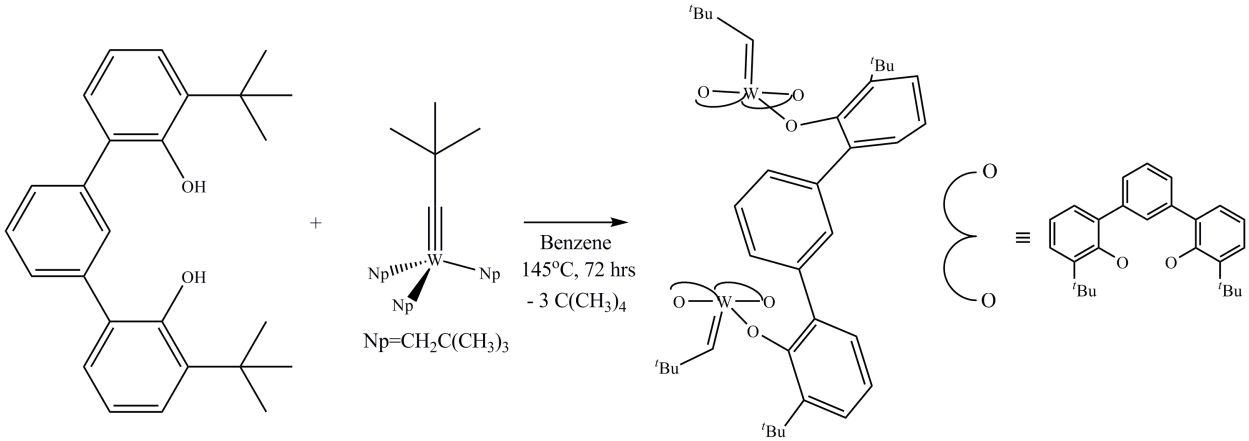


Figure 2-4: Synthesis of {[^{t}BuOCO](CH$_3$)$_3$CCH=}W(μ-^{t}BuOCHO)W{=CHC(CH$_3$)$_3$[^{t}BuOCO]} (**4** and **5**)

Owing to the high temperature required for conversion, and since W(CH$_2$C(CH$_3$)$_3$)$_3$-(≡CC(CH$_3$)$_3$) is known to decompose above 140 °C, an intractable mixture of products was obtained, and no single species could be isolated on a significant scale. Despite the complicated product mixture, the ^{1}H NMR spectrum did indicate the presence of two closely related isomers. After 16 hours, two sets of four singlets, characteristic of the four inequivalent *t*-butyl moieties in

each compound, are observed between 0.5 ppm and 2.0 ppm, in a 70:30 ratio (**4**:**5**). Compound **4** is slowly converted to **5** over 96 hours until a 90:10 ratio is reached. This corresponds to a value of $\Delta G_{145°}$=1.8 kcal/mol for the equilibrium. The reaction was stopped after 12 hours to enable study of the kinetically favored isomer. X-ray analysis of a single-crystal obtained by a slow evaporation of an Et_2O solution of the product mixture revealed the dinuclear structure **4**. The molecular structure of **5** was obtained from X-ray analysis of a single crystal obtained by the same method after 72 hours of heating (Figure 2-5).

Each compound contains two tungsten-alkylidene moieties bridged by a ^{t}BuOCHO ligand. An additional tridentate ^{t}BuOCO ligand completes the distorted square-pyramidal coordination sphere around each tungsten center. The differences between the two structures are subtle. In **4**, the bridging ligand is rotated such that the oxygen atoms of the bridging ligand are proximal to the center backbone ring of the ligand. In **5**, the arrangement is reversed, with the oxygen atoms of the bridging ligand distal to the center ring of the ligand (Figure 2-6).

The twist angles of the tridentate ^{t}BuOCO ligands differ significantly between **4** and **5**. The rings of the pendant arms are approximately coplanar in **4**, while in **5**, the pendant arms are twisted 42.43(13)° with respect to one another. This twist relieves steric congestion around the tungsten center and is likely the cause for the thermodynamic preference of **5** over **4**. The W-$C_{alkylidene}$ bond lengths and the W-$C_{alkylidene}$-C bond angles in **4** are 1.900(6) Å, 1.876(6) Å, 143.4(5)°, and 151.3(7)° respectively, and the corresponding values for **5** are 1.887(7) Å, 1.885(6) Å, 143.5(5)°, and 145.7(6)° respectively. The variation in W-$C_{alkylidene}$ bond lengths and the W-$C_{alkylidene}$-C bond angles between the two alkylidene moieties in each compound as well as the variation in W-$C_{alkylidene}$ bond lengths and the W-$C_{alkylidene}$-C bond angles between **4** and **5** is not chemically significant.

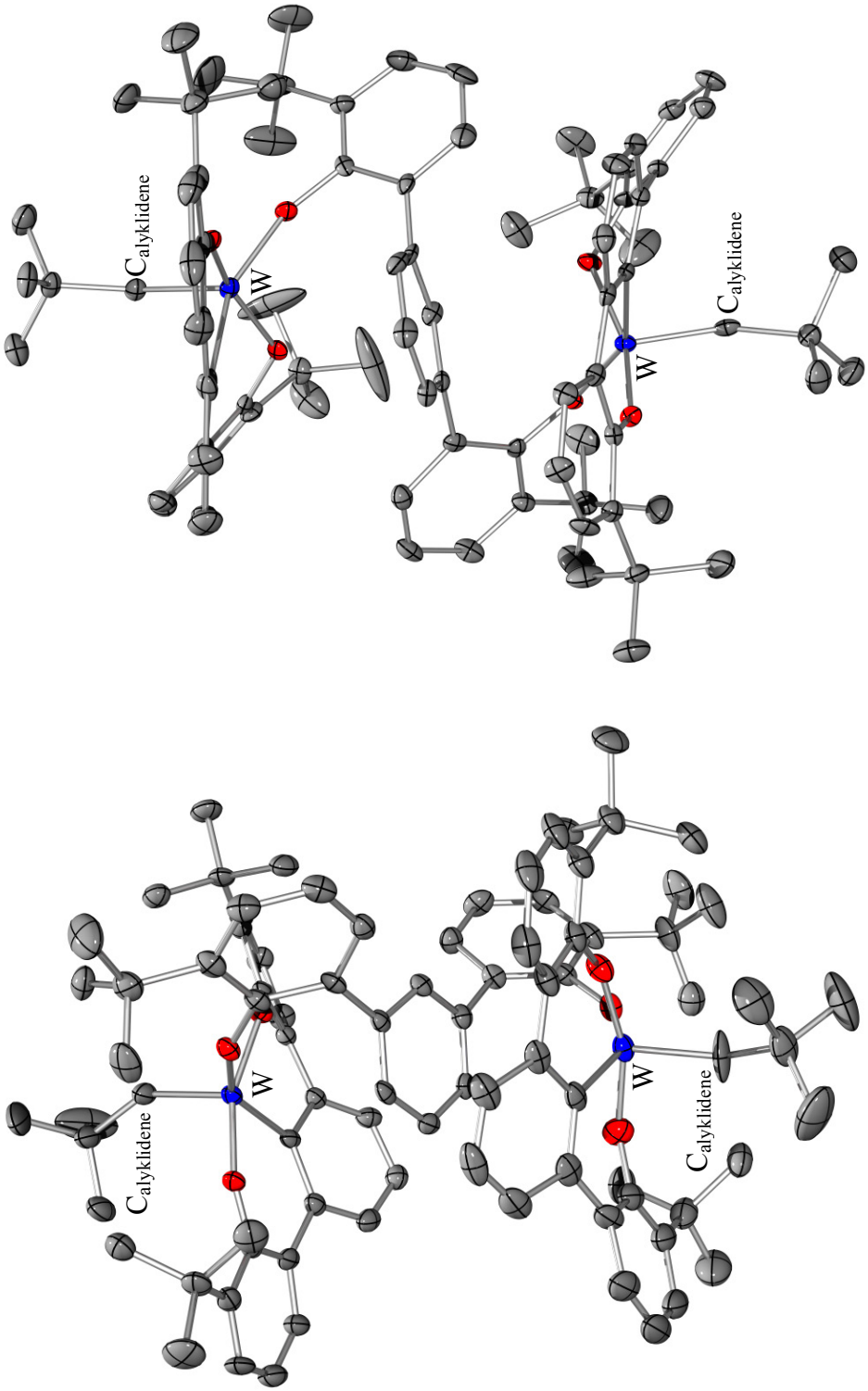


Figure 2-5: Molecular structure of **4** (left) and **5** (right). Ellipsoids are shown at 50% probability level; hydrogen atoms are omitted for clarity.

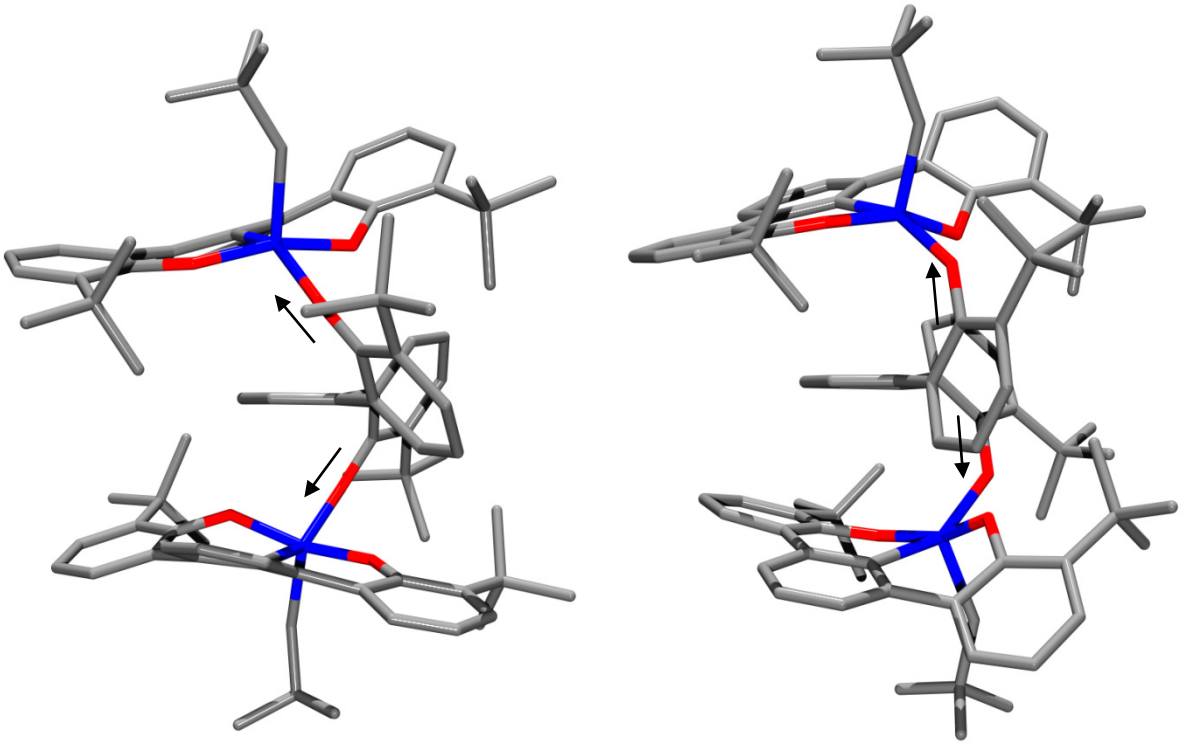


Figure 2-6: Molecular structure of **4** (left) and **5** (right) showing orientation of bridging ligand

The related reaction involving $W(CH_2TMS)_3(\equiv CTMS)$ has been attempted. During one trial with slightly impure $W(CH_2TMS)_3(\equiv CTMS)$, small, colorless crystals deposited in the NMR tube after approximately 48 hours of heating. Single-crystal X-ray analysis of one of these crystals revealed the polymeric structure $[(^tBuOCHO)Mg\{O(CH_2CH_2)_2O\}]_n$ (**6**).

The molecular structure of **6** consists of a bidentate ^{t}BuOCHO ligand and two molecules of 1,4-dioxane, creating a highly distorted tetrahedral geometry around a magnesium center (Figure 2-7). The two oxygen atoms of the ^{t}BuOCHO ligand and one 1,4-dioxane oxygen lie nearly in the same plane, with an average deviation of only 0.2034(5) Å from the best-fit plane defined by those three oxygen atoms and the magnesium atom. The remaining 1,4-dioxane oxygen is nearly perpendicular to that plane, with an average bond $O_{in\text{-}plane}$-Mg-$O_{out\text{-}of\text{-}plane}$ angle of 93.33(16)°. The chain extends along the crystallographic *a* axis.

Magnesium chloride is a byproduct of the synthesis of $W(CH_2TMS)_3(\equiv CTMS)$ and 1,4-dioxane is used to aid in its removal. During the reactions in which **6** is formed, liberation of free $SiMe_4$ is observed in the ^1H NMR spectrum. It can be inferred a reaction of excess Grignard reagent from the synthesis of $W(CH_2TMS)_3(\equiv CTMS)$ with **1** results in deprotonation of the phenolic oxygen atoms, followed by the binding of 1,4-dioxane to the magnesium atoms. The exact mechanism of formation of **6** was not studied further.

Further reactions were attempted with purified $W(CH_2TMS)_3(\equiv CTMS)$, but the ^1H NMR spectrum indicated complicated product mixtures, similar to the mixture seen during the formation of **4** and **5**. No further study was attempted of this reaction.

All attempts for direct reaction of the ^{t}BuOCO ligand did not result in the desired complex, but instead an alkylidene. This suggests that while an alkylidyne may be formed during the progress of the reaction, it is too unsaturated to be stable. Parallel research by another group member has revealed the addition of the ligand backbone C-H bond across the alkylidyne is a possible reaction route. This bond in the ligand cannot be eliminated, as it is an essential part of the ligand and therefore may rule out direct reaction of the ^{t}BuOCO ligand with a preformed alkylidyne as a feasible route to the target complex.

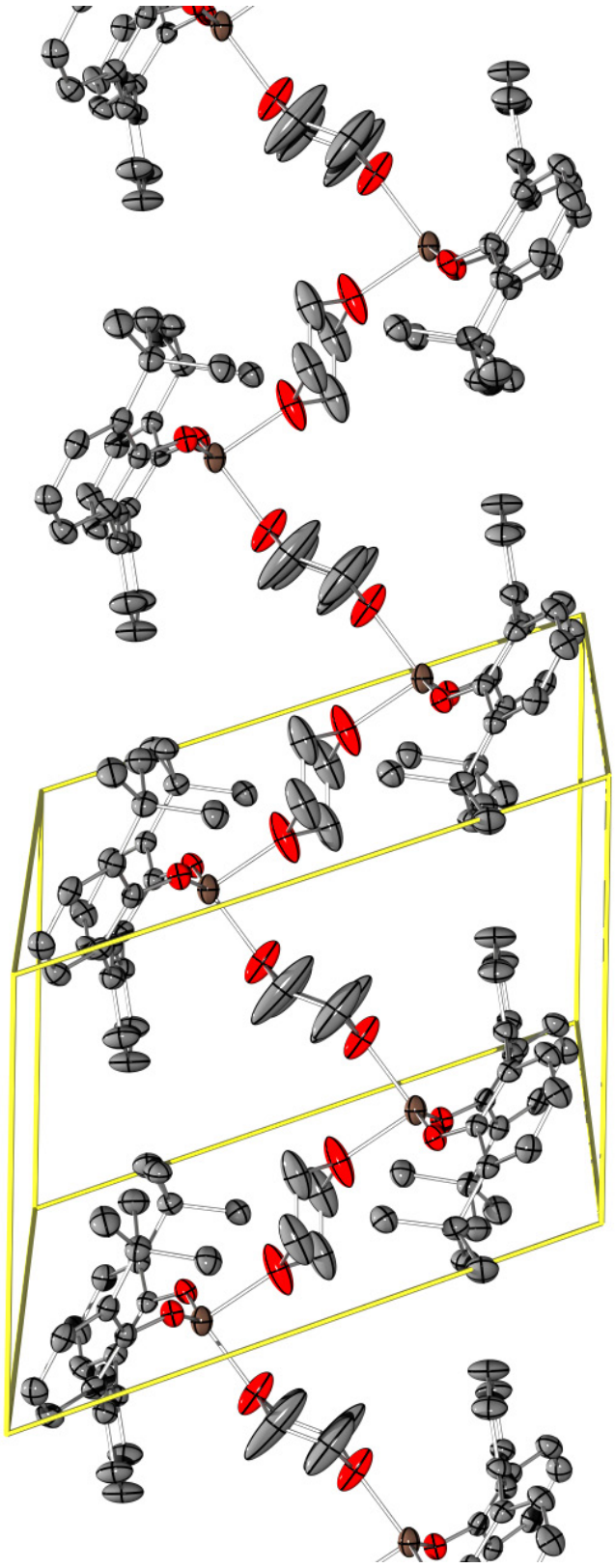
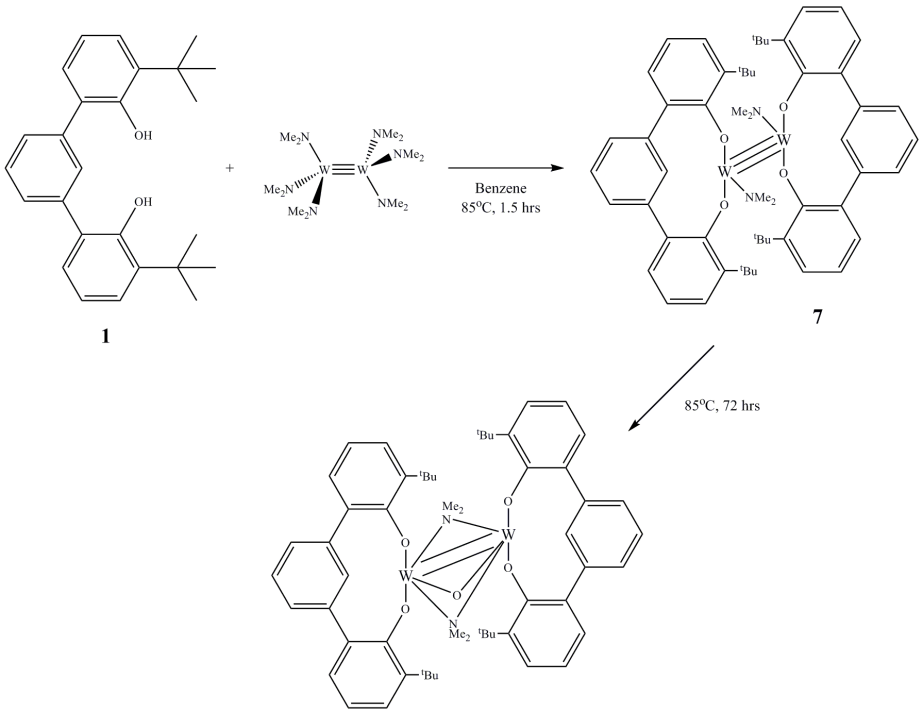


Figure 2-7: Polymeric structure of **6**. Ellipsoids are shown at 30% probability level; hydrogen atoms and benzene molecule omitted for clarity.

CHAPTER 3
PROGRESS TOWARDS COMPLEXES WITH M-M MULTIPLE BONDS SUPPORTED BY A TRIANIONIC OCO^{3-} PINCER LIGAND

Since direct reaction of **1** with alkylidyne-containing complexes did not provide the desired result, a new method was sought. Alkylidynes can be formed by metathesis reactions of W≡W containing compounds with alkynes, so an attempt was made to synthesize a compound containing **1** and such a W≡W unit. $(NMe_2)_3W{\equiv}W(NMe_2)_3$ was chosen, as it is easily prepared on an appreciable scale.[25] Treatment of $(NMe_2)_3W{\equiv}W(NMe_2)_3$ with two equivalents of **1** in hot benzene for two hours yields a dark red solution with an ^1H NMR which spectrum indicates complete conversion to **7** (Figure 3-1). Prolonged heating at 85 °C results in the formation of a green solution and precipitation of **8** as red crystals in nearly quantitative yield. Since **8** had no appreciable solubility in common NMR solvents, analysis was limited to single-crystal X-ray crystallography and combustion analysis.



1 **7** **8**

Figure 3-1: Synthesis of [^{t}BuOCHO]$(NMe_2)W{\equiv}W(NMe_2)$[^{t}BuOCHO] (**7**) and [^{t}BuOCHO]W-$(\mu\text{-}NMe_2)_2(\mu\text{-}O)$W[^{t}BuOCHO] (**8**)

^{1}H NMR was used to elucidate the structure of **7**. The spectrum shows no paramagnetic peak broadening, indicating the tungsten-tungsten triple bond is intact. Two singlets at 4.09 ppm and 2.34 ppm were each assigned to two different methyl group environments for the dimethyl amides. The *t*-butyl resonance was also split into two peaks at 1.95 ppm and 1.62 ppm. The inequivalence of these peaks indicates a staggered arrangement of the ligands bound to each tungsten center with respect to the tungsten-tungsten triple bond (Figure 3-2). The offset of the ligands creates two different chemical environments for the amide methyl groups as well as the ligand *t*-butyl groups.

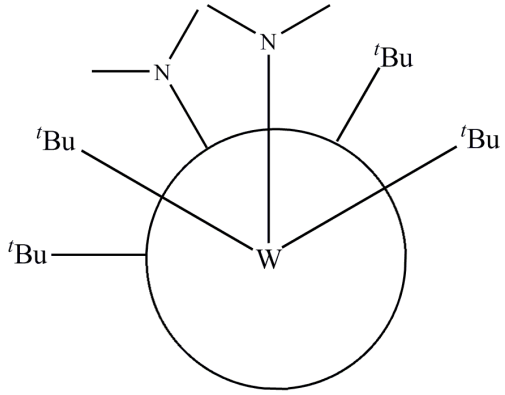


Figure 3-2: Newman projection of **7** illustrating inequivalence of *t*-butyls and amides

The molecular structure of **8** consists of two tungsten atoms bridged by two dimethylamides and an oxygen atom (Figure 3-3). The geometry around each tungsten center is distorted square-pyramidal, with a bidentate ^{t}BuOCHO moiety and the bridging amides occupying the basal positions, and the μ-O atom occupying the apical position. The average W-(μ-O) bond distance is 1.944(5) Å, similar to other reported bridging oxo compounds.[26] The 2.49726(19) Å distance between tungsten atoms is indicative of a double bond between the tungsten centers.[27]

The two possible sources of the oxygen atom are molecular oxygen and water. Both sources could oxidize one tungsten-tungsten bond, leaving the double bond observed in **8** and

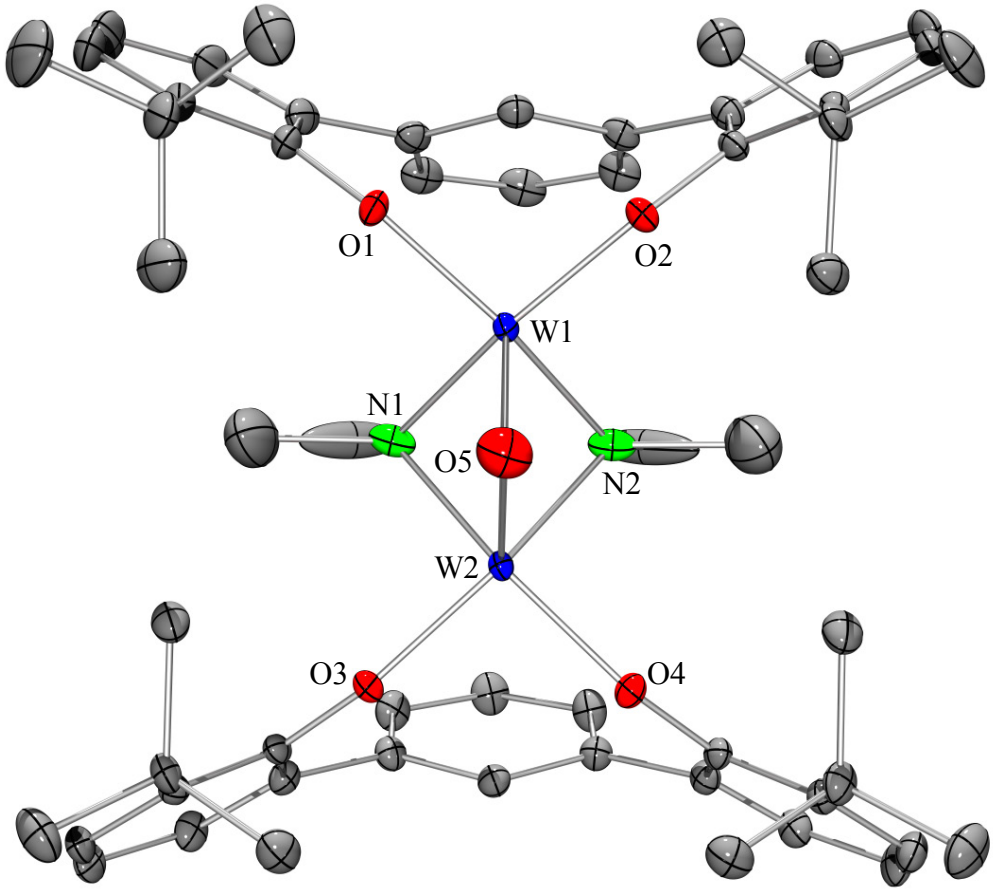


Figure 3-3: Molecular structure of **8**. Ellipsoids are shown at 30% probability level; benzene molecules and hydrogen atoms omitted for clarity.

generating a +4 oxidation state in the metals. A bridging water molecule is a possibility and could not be ruled out by X-ray crystallography.

Examples of oxidation of metal-metal bonds by molecular oxygen appear in the literature.[28] Several experiments were performed to determine the source of the oxygen atom. To eliminate molecular oxygen as the oxidant, the reaction mixture was degassed by the freeze-pump-thaw method. After 72 hours, the same green solution and red crystalline precipitate resulted. The reaction was then performed in benzene from several different sources to eliminate

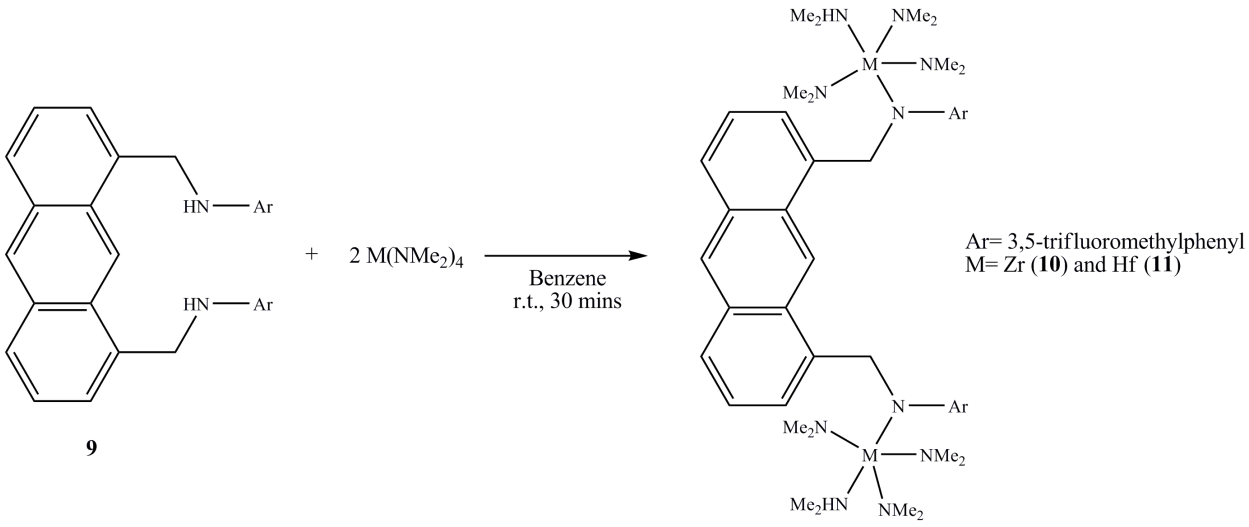
the possibility of solvent contamination. Each reaction resulted in the same reaction product. These experiments suggest molecular oxygen is not responsible for the oxidation.

To elucidate the role of water, water and toluene (as a reference) were added to C_6D_6 and the solution degassed. Combination of the two starting reagents in wet benzene yielded the same oxo-bridged complex after ten minutes. If water is not intentionally added, an additional source of water is that bound to the surface of the glass used for the reaction. The drastic increase in rate when water was added could be attributed to the relative difficulty of removing surface-bound water versus the free water present in the reaction. If the oxygen source is water and a bridging water molecule is not present, hydrogen gas must be a byproduct. There is a small peak in the ^{1}H NMR spectrum at 4.31 ppm, which could be attributed to a small amount of dissolved hydrogen gas. If the reaction vessel is thoroughly washed with D_2O and dried prior to the reaction, the peak at 4.31 ppm is not visible, which supports this hypothesis. The concentration of D_2 was too low to gain any useful information from ^{2}H NMR spectroscopy. If the NMR tube is flame-dried under vacuum prior to the reaction, a black precipitate forms within 24 hours. This suggests the compound may decompose upon extended heating if water is not present for reaction. Unfortunately, all attempts to deliberately add hydrogen to the system to confirm the identity of the peak at 4.31 ppm resulted in ligand hydrolysis.

Since all three sources of the oxygen atom have apparently been ruled out, work is continuing to attempt to determine its source.

CHAPTER 4
SYNTHESIS OF DINUCLEAR ZIRCONIUM AND HAFNIUM COMPLEXES OF A NEW ANTHRACENE DIAMIDO LIGAND

To explore the chemistry of other pincer ligands, a new NCN^{3-} pincer ligand was employed. Anthracene diamido ligand **9** was previously synthesized by M. K. Veige. Treatment of $AnthH_3$ (**9**) with a group IV metal amide of the form $M(NMe_2)_4$ (M= Zr (**10**) and Hf (**11**)) in benzene results in the formation of the dinuclear complexes $[AnthH][M(NMe_2)_3(NHMe_2)]_2$ (M = Zr, **10** and M = Hf, **11**) (Figure 4-1). The reaction is complete within ten minutes at room temperature. The structures of **10** and **11** were confirmed by a combination of ^1H and ^{13}C NMR spectroscopy, single-crystal X-ray crystallography, and combustion analysis.



9

Figure 4-1: Synthesis of $[AnthH][M(NMe_2)_3(NHMe_2)]_2$ (**10** and **11**)

In each complex, each amide donor of the AnthH ligand is bound to a metal center, resulting in a dinuclear complex. The coordination geometry around each metal atom is trigonal bipyramidal in nature, with one molecule of dimethylamine occupying the site *trans* to the ligand amide, while three dimethylamides occupy the three equatorial sites around the metal atom. ^1H NMR spectroscopy of these complexes indicates the dimethylamide and dimethylamine ligands do not exchange positions. For example, in the ^1H NMR spectrum of **11**, the methyl protons of

the three dimethylamides appear as a sharp singlet at 2.57 ppm and the methyl protons of the dimethylamine appear as a doublet at 1.45 ppm.

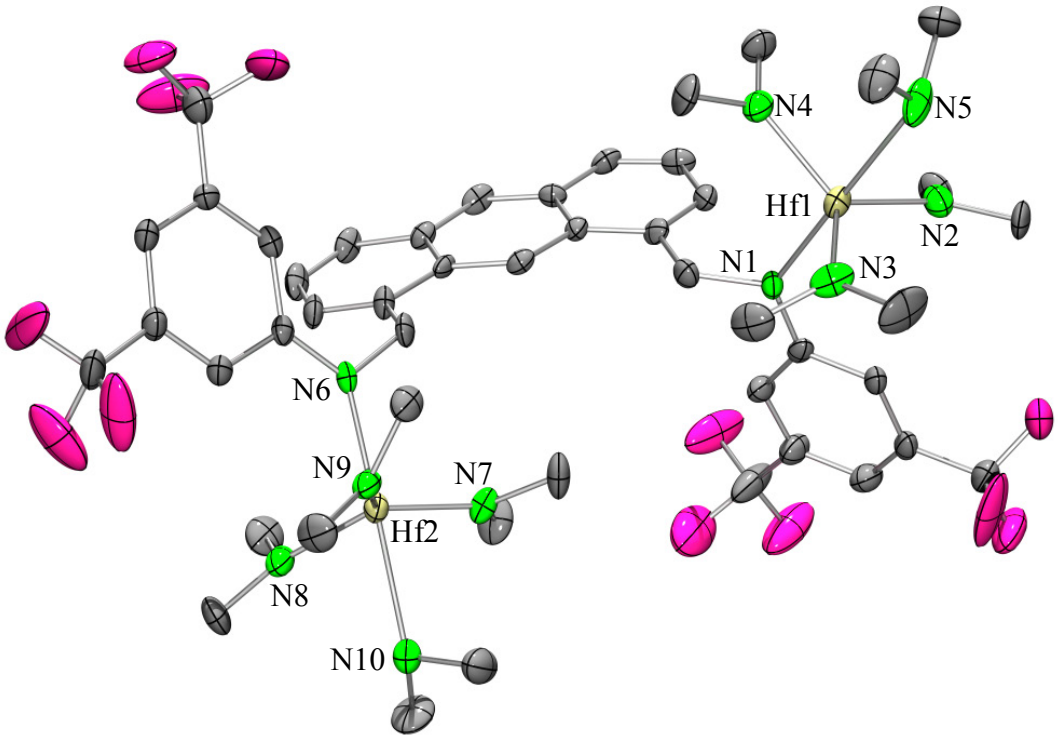


Figure 4-2: Molecular structure of **11**. Ellipsoids are shown at 30% probability level; hydrogen atoms are omitted for clarity.

A single crystal of **11** was obtained by pentane diffusion into a solution of **11** in diethyl ether and analyzed by X-ray diffraction studies (Figure 4-2). The structure exhibits trigonal bipyramidal geometry around each metal atom. The average Hf-N bond length for the dimethylamides and ligand amides is 2.041(17) Å and 2.187(10) Å, respectively, with the Hf-$NHMe_2$ bond length being longer as expected, at 2.440(11) Å. The bond angles around the hafnium atom deviate only slightly from the ideal trigonal bipyramidal values, with the average N-Hf-N angle for the equatorial dimethylamides being 119.25(7)°, and the average N-Hf-N angle between the AnthH ligand amide and the dimethylamine being 178.0(4)°. The structure of **11**

illustrates its C_2 symmetry (Figure 4-3). By viewing along the C_2 axis, the ligand arms are clearly shown as lying roughly in the plane of the anthracene backbone.

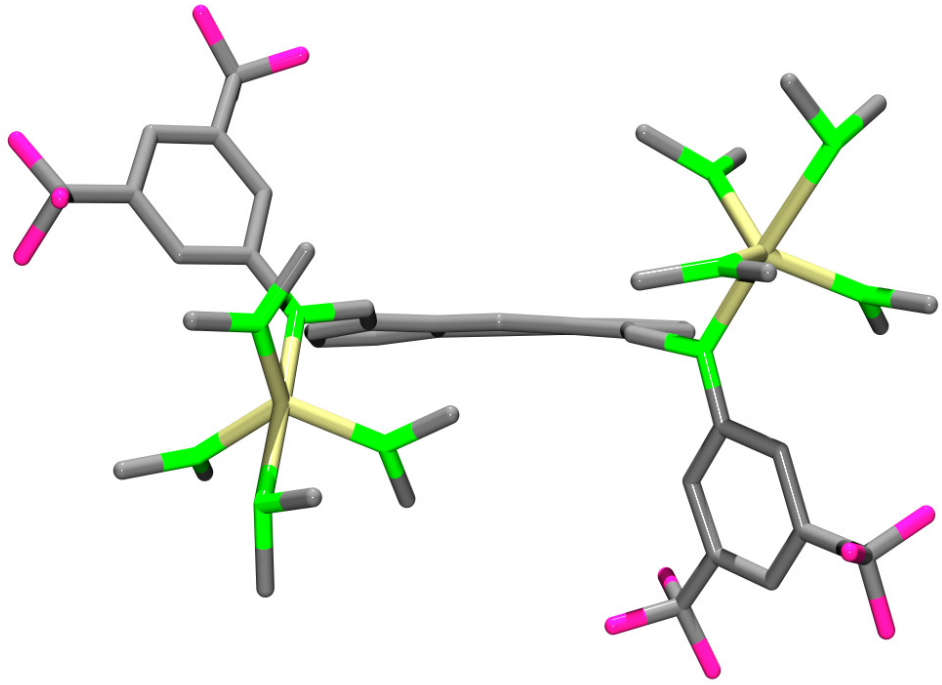


Figure 4-3: Molecular structure of **11** viewed along C_2 axis

The fact a dinuclear complex was obtained is not surprising. Other NCN pincer ligands that have been studied previously by the Veige group have often resulted in dinuclear or dimeric complexes.[29] The differences between an N-H and an O-H bond were a major reason for switching to an oxygen based pincer ligand.

CHAPTER 5
EXPERIMENTAL

General Considerations

Unless specified otherwise, all manipulations were performed under an inert atmosphere using standard Schlenk or glovebox techniques. Glassware was oven-dried before use. Pentane, toluene, diethyl ether (Et_2O), and tetrahydrofuran (THF) were dried using a Glass Contour drying column. Benzene-d_6 (Cambridge Isotopes) and benzene were dried over sodium-benzophenone ketyl and distilled or vacuum transferred and stored over 4 Å molecular sieves. NMR spectra were obtained on Varian Mercury Broad Band 300 MHz or Varian Mercury 300 MHz spectrometers. Chemical shifts are reported in δ (ppm). For ^1H and $^{13}C\{^1H\}$ NMR spectra, the residual protio solvent peak was referenced as an internal reference. Elemental analyses were performed by Complete Analysis Laboratory Inc., Parsippany, New Jersey.

Synthesis of [^{t}BuOCO]W(=CHC(CH$_3$)$_3$)(O-2,6-C$_6$H$_3$-^{i}Pr$_2$) (3)

In a 50 mL Schlenk tube, W(≡CC(CH$_3$)$_3$)(CH$_2$C(CH$_3$)$_3$)(O-2,6-C$_6$H$_3$-^{i}Pr$_2$)$_2$ (**2**) (91 mg, 0.14 mmol) was added to a solution of **1** (50 mg, 0.14 mmol) in benzene (2 mL). The mixture was heated at 85 °C for two hours. The solvent was removed *in vacuo* from the resulting dark red solution to yield **3** as a dark red oil (134 mg, 98 %) containing one equivalent of 2,6-diisopropylphenol. X-ray quality crystals were obtained from the slow evaporation of an Et_2O solution. ^1H NMR (300 MHz, C_6D_6) δ (ppm): 7.99 (d, *J*=7.9 Hz, 2H, Ar-*H*), 7.80 (dd, ^3J=7.9 Hz, ^4J=1.5 Hz, 2H, Ar-*H*), 7.38 (t, *J*=7.9 Hz, 1H, Ar-*H*), 7.33 (dd, ^3J=7.8 Hz, ^4J=1.5 Hz, 2H, Ar-*H*), 7.03 (d, *J*=1.1 Hz, 1H, phenol Ar-*H*), 7.01 (s, 1H, phenol Ar-*H*), 6.98 (s, 1H, Ar-*H*), 6.96 (s,1H, Ar-*H*), 6.91 (m, 1H, phenol Ar-*H*), 6.89 (s, 1H, Ar-*H*), 6.88 (d, *J*=3.8 Hz, 1H, Ar-*H*), 6.87 (s, 1H, Ar-*H*), 5.54 (s, $J_{H\text{-}W}$=8.7 Hz, 1H, W=C*H*C(CH$_3$)$_3$), 4.09 (sept, *J*=6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 2.93 (sept, *J*=6.9 Hz, 2H, phenol C*H*(CH$_3$)$_2$) 2.39 (sept, *J*=6.7 Hz, 1H, C*H*(CH$_3$)$_2$), 1.44 (s, 18H,

Ar-C(CH_3)$_3$), 1.42 (d, *J*=6.9Hz, 6H, CH(CH_3)$_2$), 0.84 (s, 9H, W=CHC(CH_3)$_3$), 0.69 (d, *J*=6.7 Hz, 6H, -CH(CH_3)$_2$). ^{13}C NMR (75.36 Hz, C_6D_6) δ (ppm): 272.2 (s, W=*C*HC(CH$_3$)$_3$), 182.7 (s, C aromatic), 160.3 (s, C aromatic), 158.5 (s, C aromatic), 150.8 (s, phenol C aromatic), 140.9 (s, C aromatic), 138.2 (s, C aromatic), 137.2 (s, C aromatic), 137.1 (s, C aromatic), 134.2 (s, phenol C aromatic), 133.0 (s, C aromatic), 130.0 (s, C aromatic), 126.7 (s, C aromatic), 126.4 (s, C aromatic), 124.4 (s, C aromatic), 124.2 (s, phenol C aromatic), 123.9 (s, C aromatic), 123.6 (s, C aromatic), 122.3 (s, C aromatic), 121.5 (s, phenol C aromatic), 47.9 (s, W=CH*C*(CH$_3$)$_3$), 35.6 (s, Ar-*C*(CH$_3$)$_3$), 33.3 (s, CH(*C*H$_3$)$_2$), 32.0 (s, W=CHC(*C*H$_3$)$_3$), 30.9 (s, Ar-C(*C*H$_3$)$_3$), 27.7 (s, phenol *C*H(CH$_3$)$_2$), 27.5 (s, *C*H(CH$_3$)$_2$), 23.9 (s, CH(*C*H$_3$)$_2$), 23.6 (s, *C*H(CH$_3$)$_2$), 23.3 (s, phenol Ar-CH(*C*H$_3$)$_2$). Anal. Calcd. for $C_{43}H_{54}O_3W$: C, 64.34; H, 6.78. Found: C, 64.42; H, 6.94.

Synthesis of {[^{t}BuOCO](CH$_3$)$_3$CCH=}W(μ-^{t}BuOCHO)W{=CHC(CH$_3$)$_3$[^{t}BuOCO]} (4 and 5)

In a 50 mL Schlenk tube, W(CH$_2$C(CH$_3$)$_3$)$_3$(≡CC(CH$_3$)$_3$) (200 mg, 0.534 mmol) was added to a solution of **1** (151 mg, 0.356 mmol) in benzene (2 mL). The solution was degassed. The reaction mixture was heated to 145 °C for 72 hours. Removal of solvent yielded a dark red oil. Crystalline material for X-ray analysis was obtained by slow evaporation of Et_2O.

Synthesis of [^{t}BuOCHO](NMe$_2$)W≡W(NMe$_2$)[^{t}BuOCHO] (7)

In a J. Young NMR tube, (NMe$_2$)$_3$W≡W(NMe$_2$)$_3$ (34 mg, 0.055 mmol) and **1** (40 mg, 0.11 mmol) were combined in benzene (0.5 mL). The solution was warmed to 85 °C for 1.5 hours. The dark red solution was allowed to cool to room temperature and the solvent was removed *in vacuo* to yield **7** as a dark red solid (64 mg, 97 %). ^{1}H NMR (300 MHz, C_6D_6) δ (ppm): 8.81 (s, 1H, Ar-*H*), 7.69 (s, 1H, Ar-*H*), 7.38-7.29 (m, 12H, Ar-*H*), 7.23 (s, 2H, Ar-*H*), 7.09-7.06 (m, 1H, Ar-*H*), 6.94-6.88 (m, 3H, Ar-*H*), 4.09 (s, 6H, N(CH_3)$_2$), 2.34 (s, 6H, N(CH_3)$_2$), 1.95 (s, 18H, Ar-C(CH_3)$_3$), 1.62 (s, 18H, Ar-C(CH_3)$_3$).

Synthesis of [^{t}BuOCO]W(μ-NMe$_2$)$_2$(μ-O)W[^{t}BuOCO] (8)

In a J. Young NMR tube, $(NMe_2)_3W{\equiv}W(NMe_2)_3$ (34 mg, 0.055 mmol) and **1** (40 mg, 0.11 mmol) were combined in benzene (0.5 mL). The solution was warmed to 85 °C for 72 hours. The dark green solution was decanted from a red, crystalline precipitate. The resulting solid was dried *in vacuo* to yield **7** as a green powder (50 mg, 76 %). Solid **5** had no appreciable solubility in C_6D_6, $CDCl_3$, or THF-d_8, making NMR study impossible. Anal. Calcd. for $C_{56}H_{68}N_2O_5W_2$: C, 55.27; H, 5.63; N, 2.30. Found: C, 55.49; H, 5.84; N, 2.44.

Synthesis of [AnthH][Zr(NMe$_2$)$_3$(NHMe$_2$)]$_2$ (10)

$Zr(NMe_2)_4$ (40.4 mg, 0.151 mmol) was added to a solution of $AnthH_3$ (**9**) (50.0 mg, 0.076 mmol) in benzene (1 mL), and the resulting mixture was stirred for ten minutes. Stirring was then ceased and the reaction mixture was allowed to stand at room temperature for one hour, during which time a precipitate formed. The solvent was decanted and the product dried *in vacuo* to yield **10** as a pale yellow solid (80.8 mg, 89 %). ^{1}H NMR (300 MHz, C_6D_6) δ (ppm): 9.11 (s, 1H, Ar-*H*), 8.21 (s, 1H, Ar-*H*), 7.66 (d, *J*=8.2 Hz, 2 H, Ar-*H*), 7.53 (d, *J*=6.9 Hz, 2 H, Ar-*H*), 7.30 (s, 4 H, Ar-*H*), 7.21 (m, 2 H, Ar-*H*), 7.07 (s, 2 H, Ar-*H*), 5.46 (s, 4 H, Ar-CH_2N), 2.66 (s, 32 H, Zr-N(CH_3)$_2$), 1.51 (d, *J*=6.3 Hz, 12 H, Zr-NH(CH_3)$_2$), 0.78 (sept, *J*=6.4 Hz, 2 H, Zr-N*H*(CH$_3$)$_2$). ^{13}C NMR (75.36 Hz, C_6D_6) δ (ppm): 159.5 (s, C aromatic), 136.6 (s, C aromatic), 132.8 (s, C aromatic), 132.3 (s, C aromatic), 131.8 (s, C aromatic), 130.6 (s, C aromatic), 129.4 (s, C aromatic), 127.8 (s, C aromatic), 125.8 (s, C aromatic), 125.7 (s, C aromatic), 124.1 (s, C aromatic), 116.4 (s, C aromatic), 114.6 (s, C aromatic), 106.7 (s, Ar-*C*F$_3$), 52.4 (s, Ar-*C*H$_2$N), 42.2 (s, Zr-N(*C*H$_3$)$_2$), 39.1 (s, Zr-NH(*C*H$_3$)$_2$).

Synthesis of [AnthH][Hf(NMe$_2$)$_3$(NHMe$_2$)]$_2$ (11)

$Hf(NMe_2)_4$ (53.6 mg, 0.151 mmol) was added to a solution of **9** (50.0 mg, 0.076 mmol) in benzene (1 mL), and the resulting mixture was stirred for ten minutes. Stirring was then

stopped and the reaction mixture was allowed to stand at room temperature for one hour, during which time a precipitate formed. The solvent was decanted and the solid product dried *in vacuo* to yield **11** as a pale yellow solid (90.9 mg, 87 %). ^{1}H NMR (300 MHz, C_6D_6) δ (ppm): 9.00 (s, 1H, Ar-*H*), 8.08 (s, 1H, Ar-*H*), 7.53 (d, *J*=8.8 Hz, 2H, Ar-*H*), 7.45 (d, *J*=6.6 Hz, 2H, Ar-*H*), 7.26 (s, 4H, Ar-*H*), 7.08 (m, 2H, Ar-*H*), 7.04 (s, 1H, Ar-*H*), 6.96 (s, 1H, Ar-*H*), 5.42 (s, 4, Ar-C*H*$_2$N), 2.57 (s, 32 H, Hf-N(C*H*$_3$)$_2$), 1.45 (d, *J*=6.3 Hz, 12 H, Hf-NH(C*H*$_3$)$_2$), 0.79 (sept, *J*=6.3 Hz, 2 H, Hf-N*H*(CH$_3$)$_2$). ^{13}C NMR (75.36 Hz, C_6D_6) δ (ppm): 159.5 (s, C aromatic), 136.7 (s, C aromatic), 133.1 (s, C aromatic), 132.5 (s, C aromatic), 132.1 (s, C aromatic), 130.9 (s, C aromatic), 129.8 (s, C aromatic), 128.2 (s, C aromatic), 126.0 (s, C aromatic), 124.5 (s, C aromatic), 116.6 (s, C aromatic), 115.3 (s, C aromatic), 107.8 (s, Ar-*C*F$_3$), 52.4 (s, Ar-*C*H$_2$N), 42.3 (s, Hf-N(*C*H$_3$)$_2$), 39.3 (s, Hf-NH(*C*H$_3$)$_2$).

APPENDIX A
^{1}H AND $^{13}C\{^{1}H\}$ NMR SPECTRA

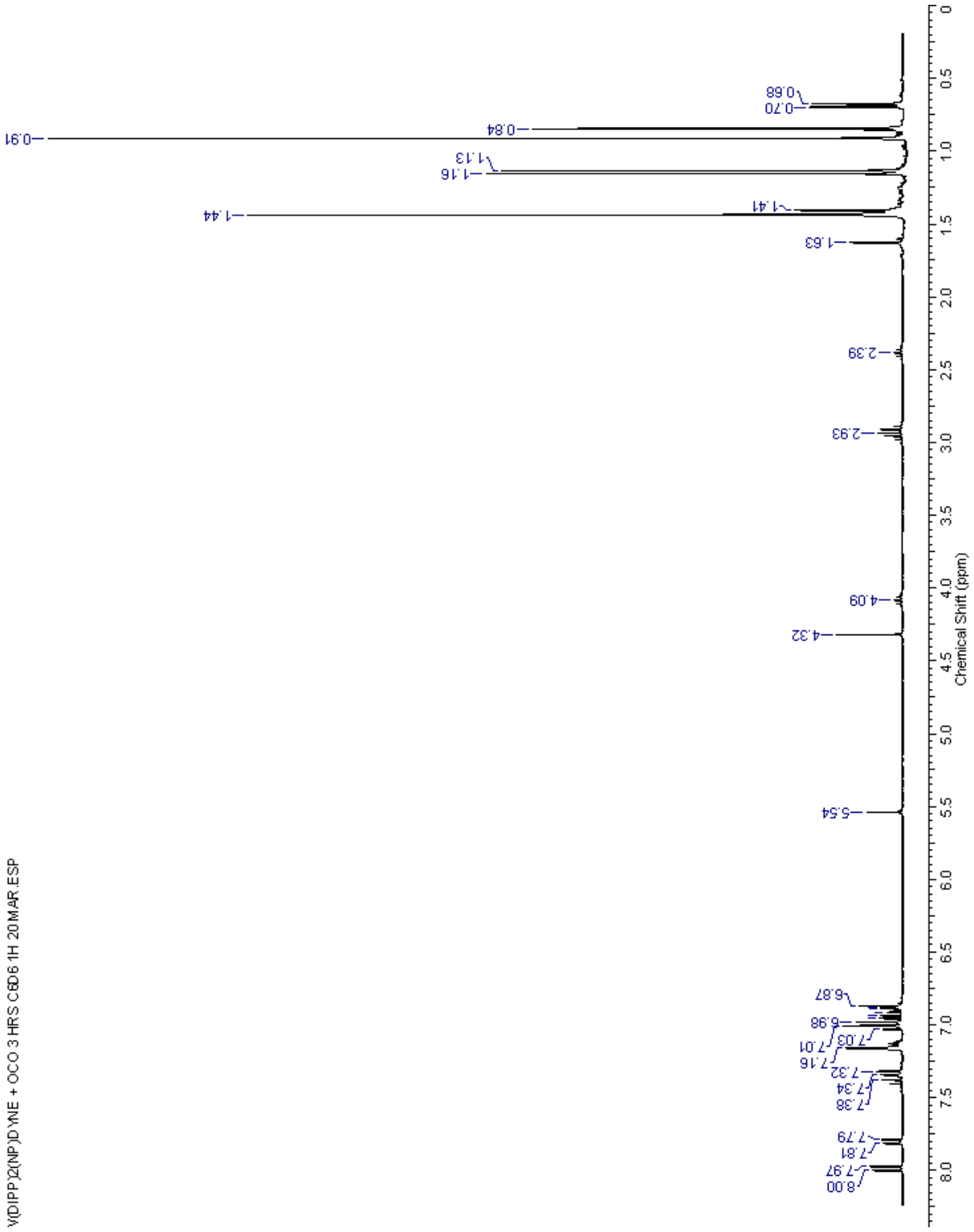


Figure A-1: ^{1}H NMR spectrum of [^{t}BuOCO]W(=CHC(CH$_3$)$_3$)(O-2,6-^{i}Pr$_2$-C$_6$H$_3$) (**3**) in C$_6$D$_6$

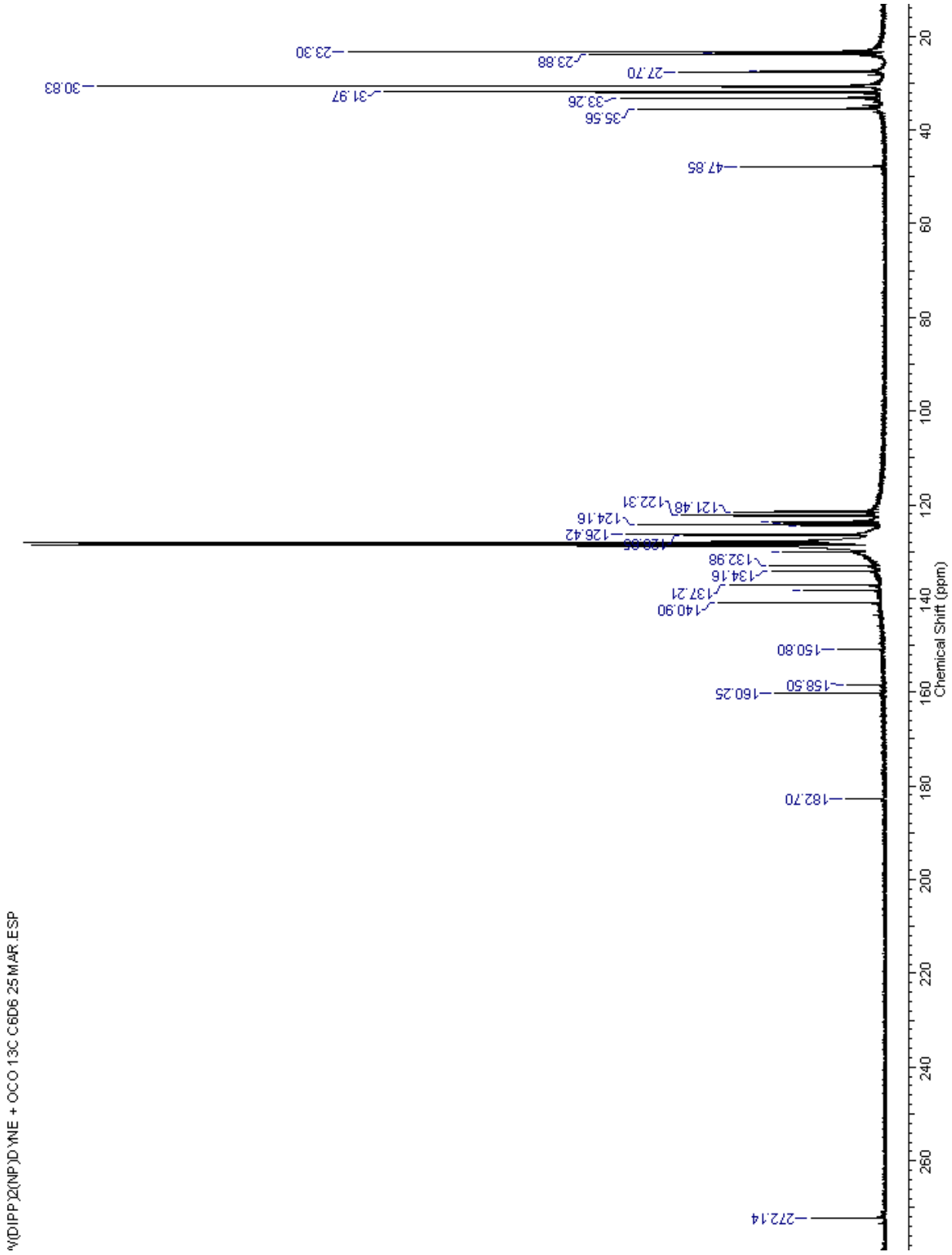


Figure A-2: $^{13}C\{^{1}H\}$ NMR spectrum of [^{t}BuOCO]W(=CHC(CH$_3$)$_3$)(O-2,6-^{i}Pr$_2$-C$_6$H$_3$) (**3**) in C_6D_6

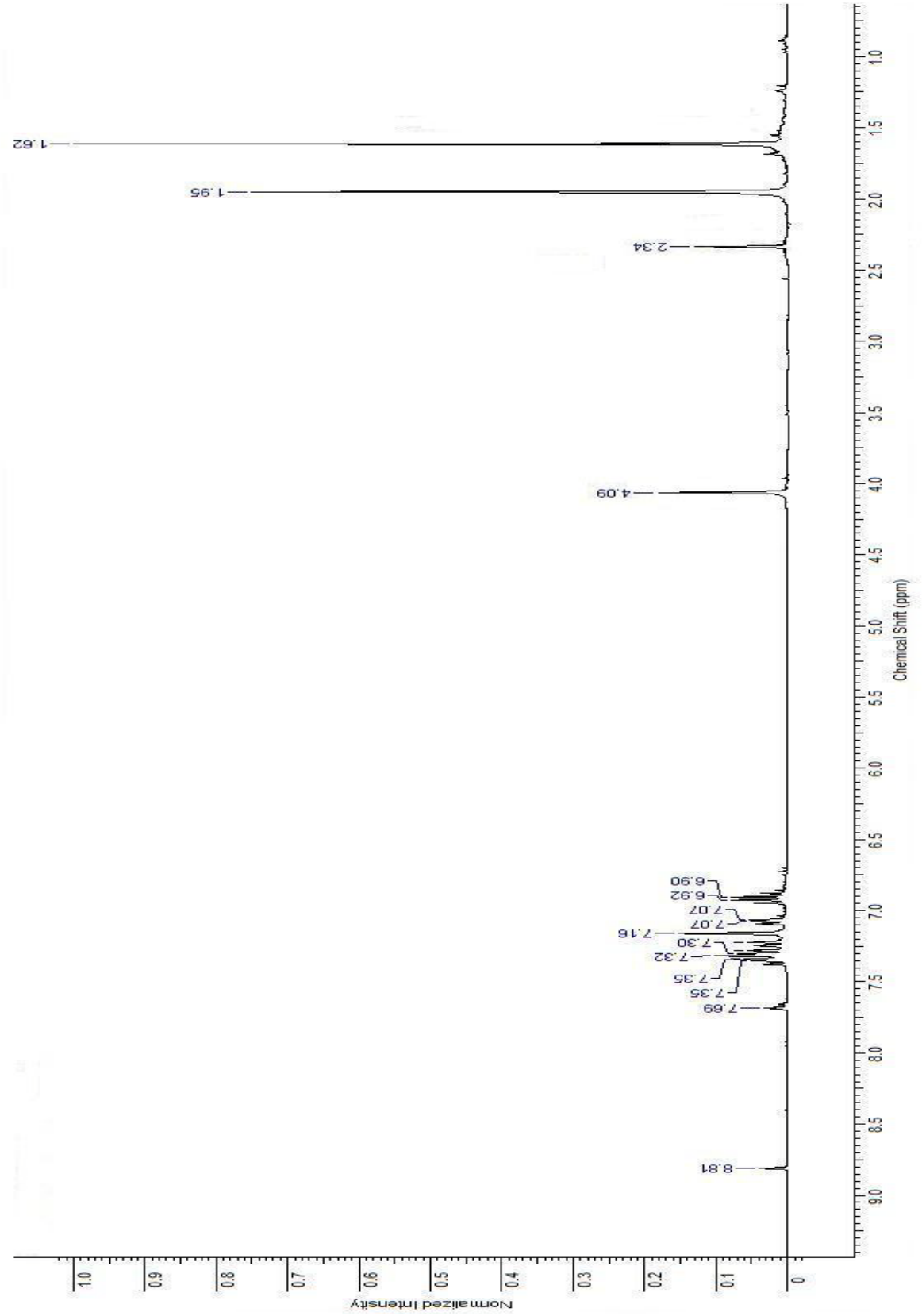


Figure A-3: ^{1}H NMR spectrum of [^{t}BuOCHO](NMe$_2$)W≡W(NMe$_2$)[^{t}BuOCHO] (**7**) in C_6D_6

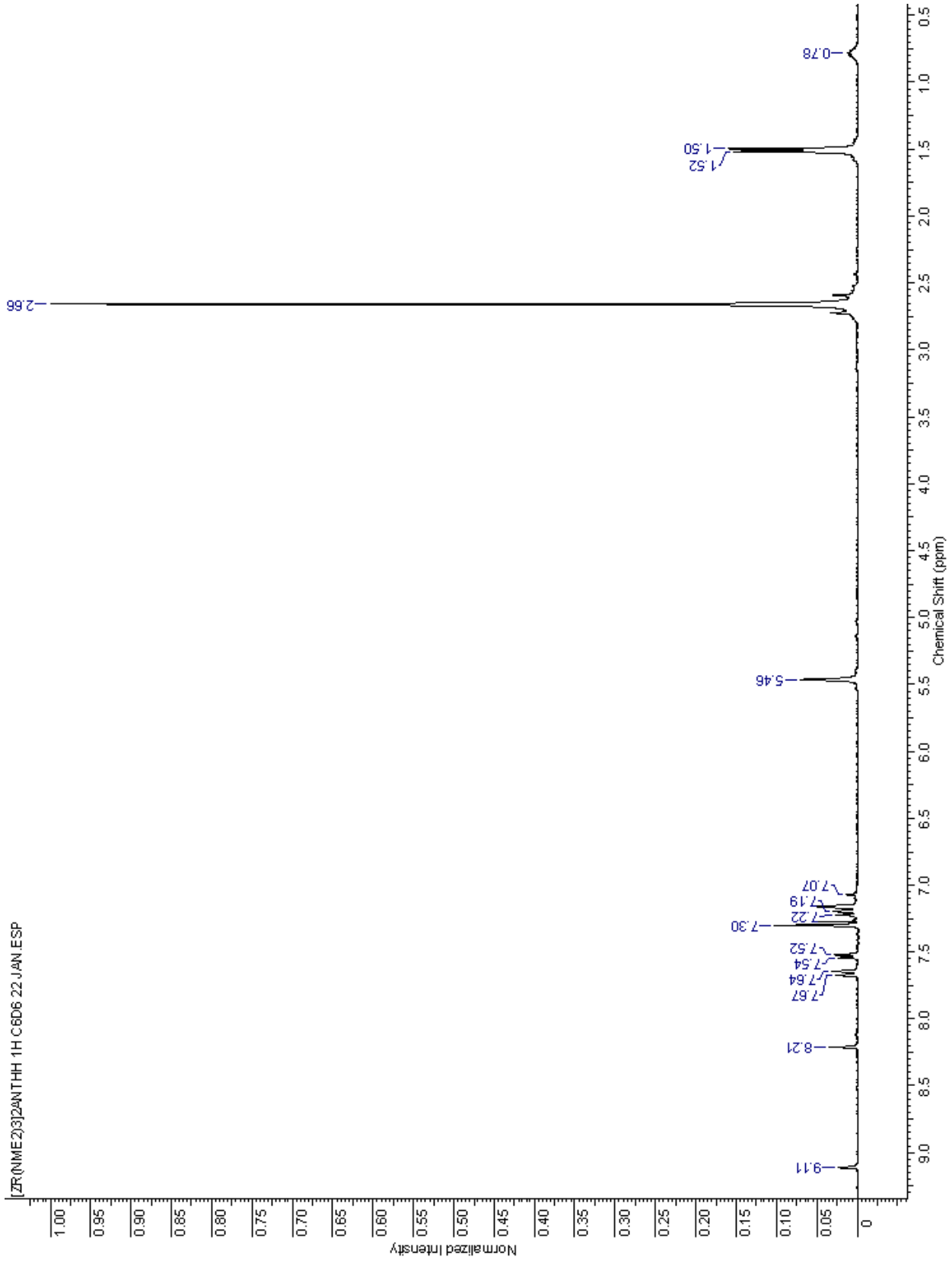


Figure A-4: ^{1}H NMR spectrum of [AnthH][Zr(NMe$_2$)$_3$(NHMe$_2$)]$_2$ (**10**) in C_6D_6

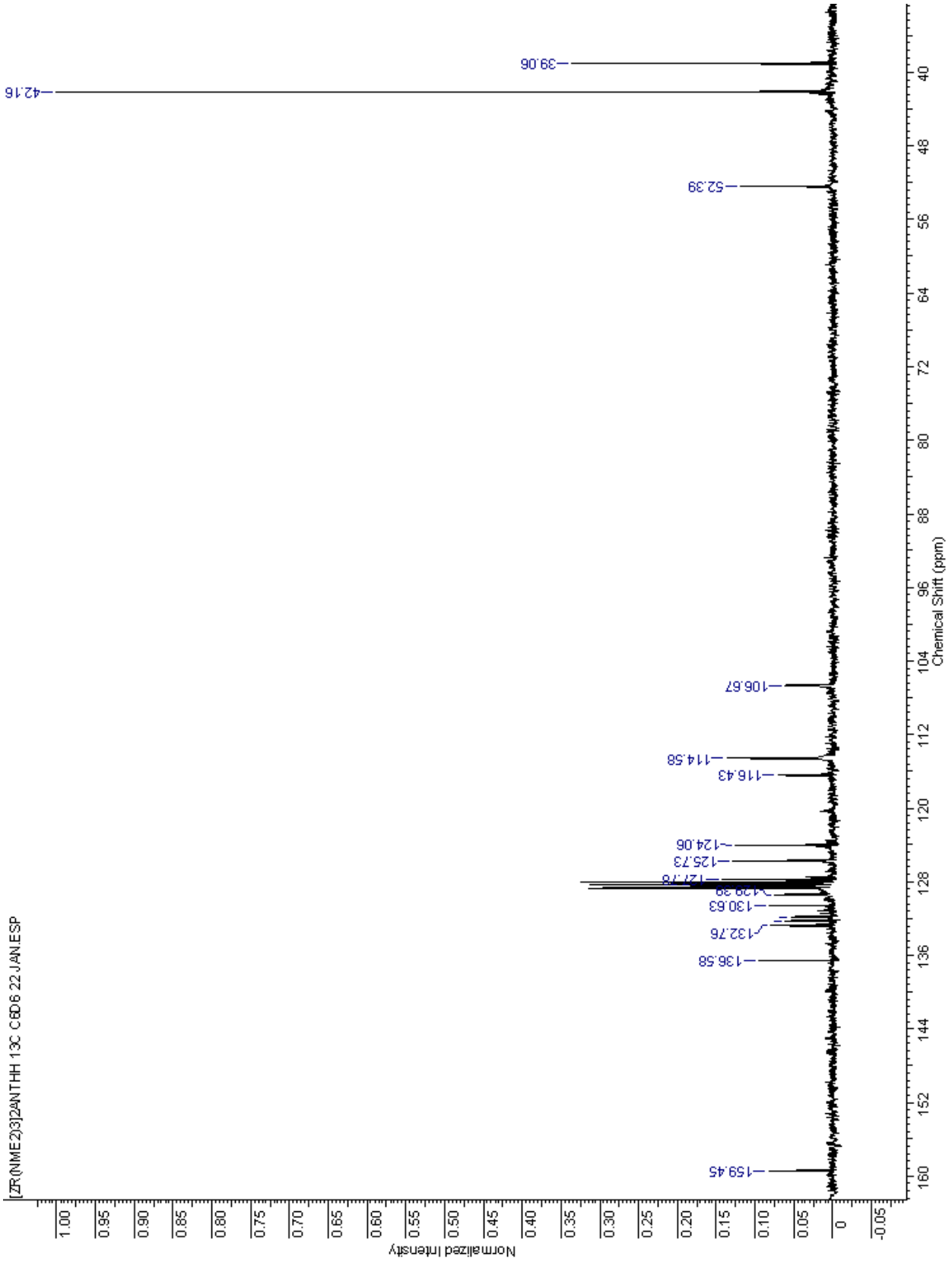


Figure A-5: $^{13}C\{^{1}H\}$ NMR spectrum of $[AnthH][Zr(NMe_2)_3(NHMe_2)]_2$ (**10**) in C_6D_6

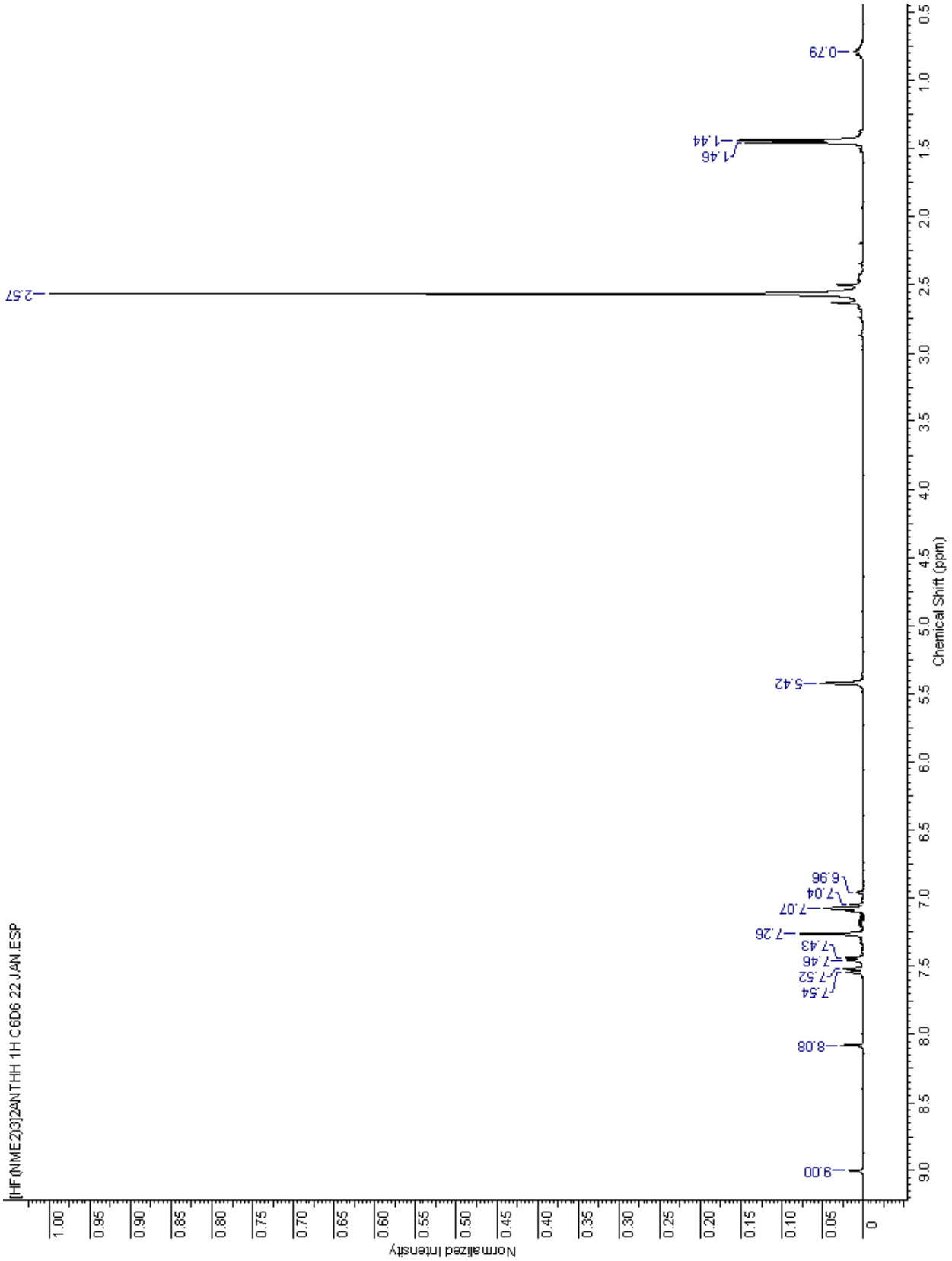


Figure A-6: ^{1}H NMR spectrum of [AnthH][Hf(NMe$_2$)$_3$(NHMe$_2$)]$_2$ (**11**) in C_6D_6

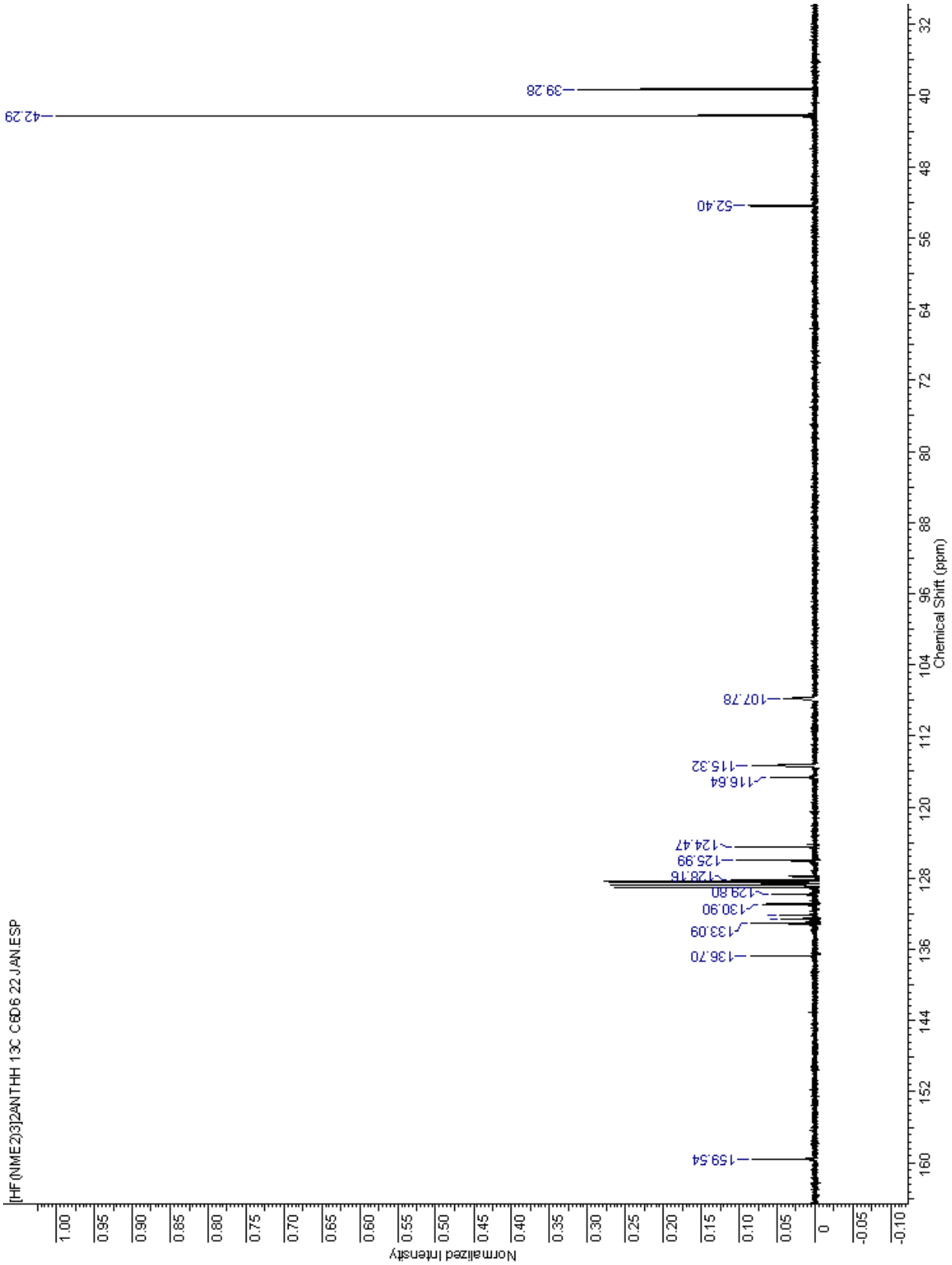


Figure A-7: $^{13}C\{^{1}H\}$ NMR spectrum of $[AnthH][Hf(NMe_2)_3(NHMe_2)]_2$ (**11**) in C_6D_6

APPENDIX B
X-RAY STRUCTURAL DATA AND TABLES

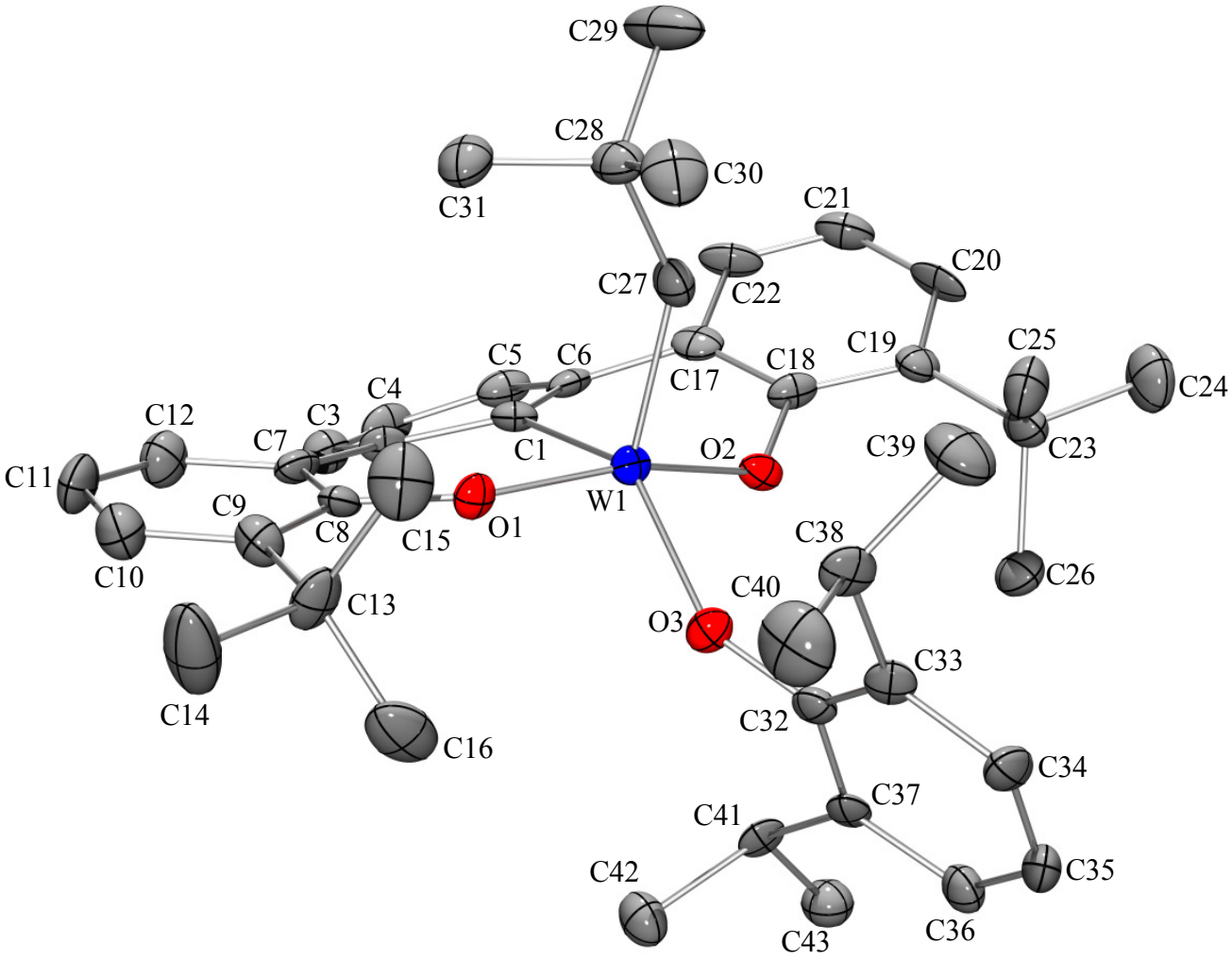


Figure B-1: Molecular structure of [^{t}BuOCO]W(=CHC(CH$_3$)$_3$)(O-2,6-^{i}Pr$_2$-C$_6$H$_3$) (**3**). Ellipsoids shown at the 30% probability level; hydrogens are omitted for clarity.

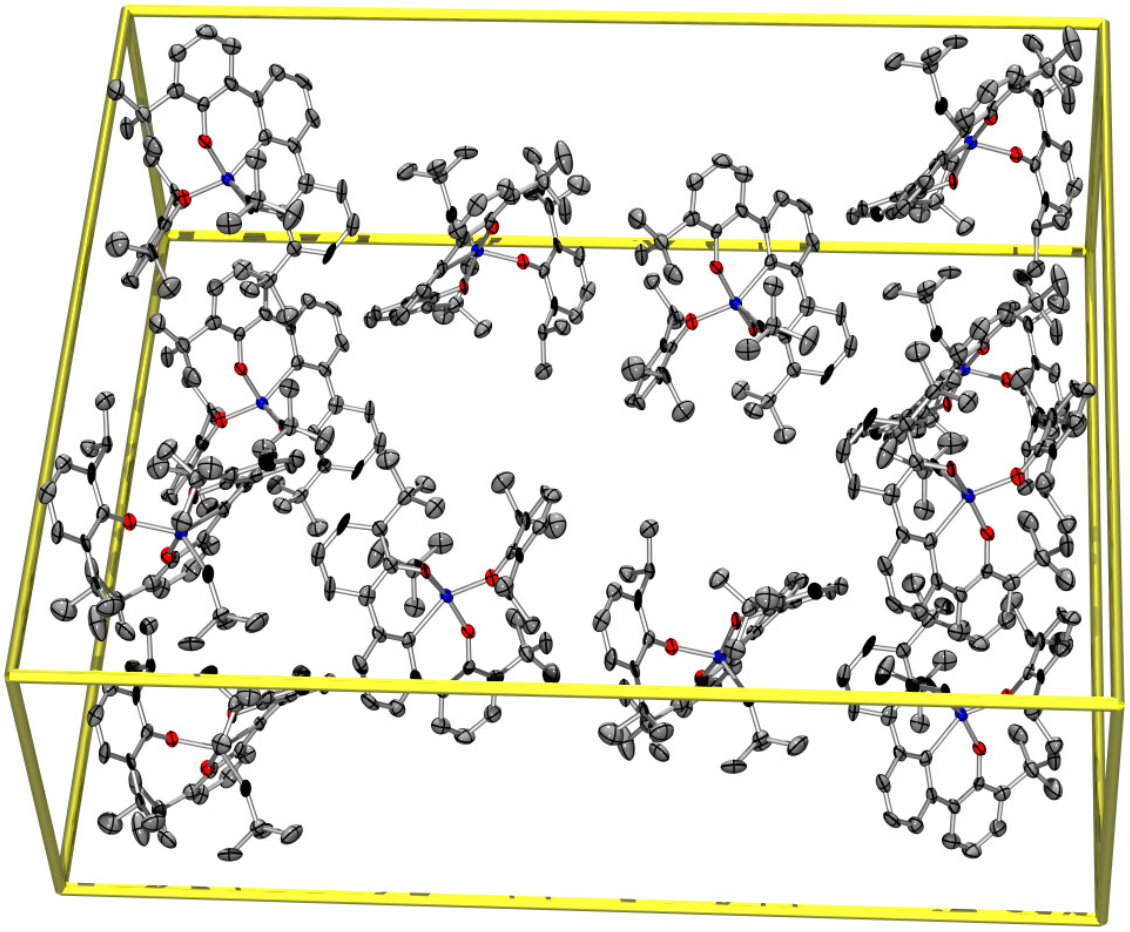


Figure B-2: Packing diagram for **3**

X-ray Experimental for [^{t}BuOCO]W(=CHC(CH$_3$)$_3$)(O-2,6-^{i}Pr$_2$-C$_6$H$_3$) (3)

Data were collected at 173 K on a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing MoKα radiation (λ = 0.71073 Å). Cell parameters were refined using up to 8192 reflections. A full sphere of data (1850 frames) was collected using the ω-scan method (0.3°frame width). The first 50 frames were re-measured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was < 1 %). Absorption corrections by integration were applied based on measured indexed crystal faces.

The structure was solved by the author using Direct Methods in *SHELXTL6,* and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. A total of 847 parameters were refined in the final cycle of refinement using 10217 reflections (with I > 2σI) to yield R_1 and wR_2 of 5.00% and 11.27%, respectively. Refinement was done using F^2.

Table B-1: Crystal data, structure solution, and refinement for [^{t}BuOCO]W(=CHC(CH$_3$)$_3$)(O-2,6-^{i}Pr$_2$-C$_6$H$_3$) (**3**)

identification code	pelo5
empirical formula	$C_{43}H_{54}O_3W$
formula weight	802.71
T (K)	173(2)
λ (Å)	0.71073
crystal system	Monoclinic
space group	C(2)/c
a (Å)	39.001(2)
b (Å)	12.5405(8)
c (Å)	31.4372(19)
α (deg)	90
β (deg)	90.2150(10)
γ (deg)	90
V (Å^3)	15375.5(16)
Z	8
ρ_{calcd} (g mm^{-3})	1.387
crystal size (mm)	0.12 x 0.04 x 0.04
abs coeff (mm^{-1})	3.041
F(000)	6560
θ range for data collection	1.04 to 28.03
limiting indicies	$-34 \le h \le 51$, $-16 \le k \le 16$, $-41 \le l \le 39$
no. of reflns collcd	53157
no. of ind reflns	18457 [R(int) = 0.0842]
completeness to θ = 28.03°	99.1 %
absorption corr	Integration
refinement method	Full-matrix least-squares on F^2
data / restraints / parameters	18457 / 0 / 847
$R1$, $wR2$ [I > 2σ]	R1 = 0.0500, wR2 = 0.1127
$R1$, $wR2$ (all data)	R1 = 0.1139, wR2 = 0.1343
GOF on F^2	1.003
largest diff. peak and hole (e.Å^{-3})	1.022 and -0.886

$R1 = \Sigma(||F_o| - |F_c||) / \Sigma|F_o|$

$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

$S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$

$w = 1/[\sigma^2(F_o^2)+(m*p)^2+n*p]$, $p = [\max(F_o^2,0)+ 2* F_c^2]/3$, m & n are constants.

Table B-2: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for [^{t}BuOCO]W(=CHC$(CH_3)_3$)(O-2,6-^{i}Pr$_2$-C_6H_3) (**3**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	**X**	**Y**	**Z**	**U(eq)**
W1	1336(1)	-376(1)	2115(1)	28(1)
W2	1408(1)	4970(1)	4355(1)	27(1)
O1	1148(1)	-1694(4)	2209(2)	33(1)
O2	1501(1)	1010(4)	2202(2)	31(1)
O3	885(1)	271(4)	2046(2)	36(1)
O4	1533(1)	6435(4)	4253(2)	31(1)
O5	1260(1)	3607(4)	4262(2)	32(1)
O6	946(1)	5498(4)	4435(2)	35(1)
C1	1680(2)	-812(6)	2627(2)	32(2)
C2	1616(2)	-1738(6)	2882(3)	32(2)
C3	1772(2)	-1818(7)	3286(3)	42(2)
C4	2002(2)	-1066(7)	3429(3)	46(2)
C5	2091(2)	-228(7)	3167(3)	42(2)
C6	1934(2)	-88(6)	2772(2)	33(2)
C7	1392(2)	-2663(7)	2767(3)	37(2)
C8	1145(2)	-2620(6)	2444(3)	32(2)
C9	909(2)	-3407(7)	2349(3)	42(2)
C10	942(2)	-4350(7)	2580(3)	51(3)
C11	1203(3)	-4460(7)	2881(3)	57(3)
C12	1411(3)	-3644(7)	2979(3)	50(2)
C13	619(2)	-3260(7)	2028(3)	49(3)
C14	389(3)	-4242(9)	2027(4)	93(5)
C15	751(3)	-3111(8)	1580(3)	61(3)
C16	402(2)	-2319(9)	2161(3)	70(3)
C17	2047(2)	849(7)	2523(3)	40(2)
C18	1821(2)	1407(6)	2252(3)	34(2)

Table B-2: Continued

Atom	X	Y	Z	U(eq)
C19	1917(2)	2381(7)	2048(3)	37(2)
C20	2255(2)	2730(7)	2108(3)	44(2)
C21	2492(2)	2162(8)	2363(3)	50(3)
C22	2389(2)	1266(8)	2564(3)	47(2)
C23	1662(2)	3025(7)	1779(3)	45(2)
C24	1829(3)	4038(7)	1591(3)	66(3)
C25	1524(2)	2372(7)	1393(3)	53(3)
C26	1363(2)	3371(7)	2049(3)	55(3)
C27	1627(2)	-648(7)	1638(3)	36(2)
C28	1743(2)	-1561(7)	1364(3)	41(2)
C29	2100(3)	-1359(8)	1212(4)	80(4)
C30	1501(3)	-1601(8)	972(3)	64(3)
C31	1741(2)	-2621(7)	1599(3)	52(3)
C32	685(2)	1045(6)	1905(3)	33(2)
C33	573(2)	1086(6)	1476(3)	35(2)
C34	363(2)	1940(7)	1346(3)	45(2)
C35	275(2)	2727(7)	1635(3)	45(2)
C36	374(2)	2673(6)	2053(3)	39(2)
C37	580(2)	1824(7)	2204(3)	35(2)
C38	661(2)	207(7)	1164(3)	41(2)
C39	347(3)	-452(9)	1043(4)	83(4)
C40	848(3)	614(8)	769(3)	69(3)
C41	668(2)	1688(6)	2670(3)	34(2)
C42	442(2)	838(7)	2880(3)	45(2)
C43	665(2)	2729(7)	2929(3)	51(3)
C44	1761(2)	4615(6)	3861(2)	30(2)
C45	2021(2)	5365(6)	3760(2)	30(2)

Table B-2: Continued

Atom	X	Y	Z	U(eq)
C46	2219(2)	5272(7)	3390(3)	41(2)
C47	2161(2)	4419(7)	3110(3)	45(2)
C48	1929(2)	3644(7)	3211(3)	40(2)
C49	1734(2)	3686(6)	3591(3)	32(2)
C50	2109(2)	6287(6)	4039(2)	29(2)
C51	1861(2)	6831(6)	4272(2)	30(2)
C52	1925(2)	7756(6)	4515(2)	30(2)
C53	2264(2)	8049(7)	4541(3)	40(2)
C54	2526(2)	7521(7)	4319(3)	40(2)
C55	2450(2)	6653(7)	4076(3)	38(2)
C56	1650(2)	8382(7)	4742(3)	38(2)
C57	1466(2)	7711(7)	5081(3)	44(2)
C58	1381(2)	8766(7)	4413(3)	47(2)
C59	1782(2)	9368(7)	4956(3)	57(3)
C60	1505(2)	2763(6)	3669(2)	33(2)
C61	1264(2)	2740(6)	4001(3)	28(2)
C62	1039(2)	1900(6)	4083(3)	35(2)
C63	1067(2)	1005(7)	3821(3)	42(2)
C64	1304(2)	981(6)	3508(3)	39(2)
C65	1525(2)	1826(7)	3429(3)	40(2)
C66	751(2)	1977(7)	4418(3)	44(2)
C67	518(2)	979(8)	4410(4)	70(3)
C68	519(2)	2930(7)	4317(3)	56(3)
C69	901(2)	2093(7)	4867(3)	48(2)
C70	1729(2)	4827(6)	4805(2)	33(2)
C71	1956(2)	4021(6)	5021(3)	37(2)
C72	1942(3)	4181(8)	5494(3)	76(4)

Table B-2: Continued

Atom	X	Y	Z	U(eq)
C73	2323(2)	4220(8)	4860(4)	66(3)
C74	1847(2)	2870(6)	4903(3)	53(3)
C75	729(2)	6254(6)	4575(3)	38(2)
C76	607(2)	7021(7)	4292(3)	40(2)
C77	391(2)	7817(8)	4446(3)	54(3)
C78	296(3)	7808(9)	4863(4)	65(3)
C79	402(2)	7019(8)	5138(3)	54(3)
C80	620(2)	6214(7)	4999(3)	40(2)
C81	695(2)	6940(8)	3828(3)	53(3)
C82	653(3)	7952(9)	3573(3)	77(4)
C83	463(3)	6054(10)	3635(3)	83(4)
C84	719(2)	5313(8)	5295(3)	50(2)
C85	920(3)	5694(9)	5675(3)	80(4)
C86	410(3)	4683(9)	5446(4)	80(4)

Table B-3: Bond lengths (in Å) for [^{t}BuOCO]W(=CHC(CH$_3$)$_3$)(O-2,6-^{i}Pr$_2$-C$_6$H$_3$) (**3**)

Bond	**Length**	**Bond**	**Length**
W1-O1	1.832(5)	C5-C6	1.395(10)
W1-O2	1.872(5)	C6-C17	1.480(12)
W1-C27	1.917(8)	C7-C8	1.399(10)
W1-O3	1.946(5)	C7-C12	1.401(11)
W1-C1	2.160(8)	C8-C9	1.381(11)
W2-O5	1.827(5)	C9-C10	1.393(12)
W2-C70	1.895(8)	C9-C13	1.525(12)
W2-O4	1.928(5)	C10-C11	1.395(12)
W2-O6	1.938(5)	C11-C12	1.340(12)
W2-C44	2.124(8)	C13-C16	1.511(13)
O1-C8	1.376(9)	C13-C15	1.515(13)
O2-C18	1.356(9)	C13-C14	1.522(13)
O3-C32	1.322(9)	C17-C18	1.408(11)
O4-C51	1.373(9)	C17-C22	1.438(11)
O5-C61	1.363(9)	C18-C19	1.429(11)
O6-C75	1.345(9)	C19-C20	1.403(11)
C1-C6	1.419(11)	C19-C23	1.533(12)
C1-C2	1.434(11)	C20-C21	1.411(12)
C2-C3	1.412(10)	C21-C22	1.351(12)
C2-C7	1.495(11)	C23-C26	1.509(12)
C3-C4	1.375(12)	C23-C24	1.546(12)
C4-C5	1.382(12)	C23-C25	1.558(12)

Table B-4: Bond angles (in deg) for [^{t}BuOCO]W(=CHC(CH$_3$)$_3$)(O-2,6-^{i}Pr$_2$-C$_6$H$_3$) (**3**)

Bond	Angle	Bond	Angle
O1-W1-O2	162.0(2)	O6-W2-C44	140.5(2)
O1-W1-C27	101.7(3)	C8-O1-W1	148.5(5)
O2-W1-C27	94.3(3)	C18-O2-W1	132.3(5)
O1-W1-O3	91.9(2)	C32-O3-W1	151.0(5)
O2-W1-O3	86.5(2)	C51-O4-W2	125.0(4)
C27-W1-O3	121.6(3)	C61-O5-W2	146.9(5)
O1-W1-C1	84.2(3)	C75-O6-W2	150.3(5)
O2-W1-C1	85.2(3)	C6-C1-C2	117.5(7)
C27-W1-C1	99.7(3)	C6-C1-W1	120.6(6)
O3-W1-C1	138.3(3)	C2-C1-W1	120.8(5)
O5-W2-C70	103.7(3)	C3-C2-C1	119.1(7)
O5-W2-O4	161.0(2)	C3-C2-C7	114.4(7)
C70-W2-O4	92.7(3)	C1-C2-C7	126.6(7)
O5-W2-O6	92.7(2)	C4-C3-C2	121.7(8)
C70-W2-O6	123.2(3)	C3-C4-C5	119.5(8)
O4-W2-O6	86.2(2)	C4-C5-C6	121.1(8)
O5-W2-C44	83.8(3)	C5-C6-C1	120.7(8)
C70-W2-C44	95.6(3)	C5-C6-C17	116.1(8)
O4-W2-C44	85.1(3)	C1-C6-C17	123.2(7)
C8-C7-C12	114.4(8)	O2-C18-C19	120.3(7)
C8-C7-C2	123.0(7)	C17-C18-C19	122.2(8)
C12-C7-C2	122.6(8)	C20-C19-C18	116.9(8)
O1-C8-C9	119.7(7)	C20-C19-C23	121.2(8)
O1-C8-C7	114.5(7)	C18-C19-C23	121.9(7)
C9-C8-C7	125.8(8)	C19-C20-C21	122.0(8)
C8-C9-C10	115.8(8)	C22-C21-C20	119.4(9)
C8-C9-C13	123.3(8)	C21-C22-C17	122.5(9)
C10-C9-C13	120.8(8)	C26-C23-C19	109.9(8)

Table B-4: Continued

Bond	Angle	Bond	Angle
C9-C10-C11	120.1(9)	C26-C23-C24	107.8(7)
C12-C11-C10	121.3(9)	C19-C23-C24	111.8(8)
C11-C12-C7	122.1(9)	C26-C23-C25	108.9(8)
C16-C13-C15	110.7(8)	C19-C23-C25	112.0(7)
C16-C13-C14	107.7(9)	C24-C23-C25	106.2(8)
C15-C13-C14	107.5(9)	C28-C27-W1	139.9(7)
C16-C13-C9	109.1(8)	C29-C28-C27	109.7(7)
C15-C13-C9	111.9(8)	C29-C28-C31	108.1(8)
C14-C13-C9	109.8(8)	C27-C28-C31	112.7(8)
C18-C17-C22	116.8(9)	C29-C28-C30	108.6(9)
C18-C17-C6	121.9(8)	C27-C28-C30	107.2(7)
C22-C17-C6	121.2(8)	C31-C28-C30	110.6(7)
O2-C18-C17	117.5(8)	O3-C32-C33	121.8(7)
O3-C32-C37	117.1(7)	C44-C45-C50	123.0(7)
C33-C32-C37	121.1(7)	C47-C46-C45	119.7(8)
C34-C33-C32	118.8(8)	C48-C47-C46	120.1(8)
C34-C33-C38	120.0(8)	C47-C48-C49	121.8(8)
C32-C33-C38	121.2(7)	C48-C49-C44	119.1(7)
C35-C34-C33	119.8(8)	C48-C49-C60	115.9(7)
C36-C35-C34	121.6(8)	C44-C49-C60	124.9(7)
C35-C36-C37	121.1(8)	C51-C50-C55	116.9(7)
C36-C37-C32	117.5(8)	C51-C50-C45	122.0(7)
C36-C37-C41	122.5(8)	C55-C50-C45	121.0(7)
C32-C37-C41	119.9(7)	O4-C51-C50	116.6(7)
C33-C38-C39	111.9(7)	O4-C51-C52	118.8(7)
C33-C38-C40	113.0(8)	C50-C51-C52	124.5(8)
C39-C38-C40	111.1(8)	C53-C52-C51	114.7(7)

Table B-4: Continued

Bond	Angle	Bond	Angle
C37-C41-C42	111.4(6)	C69-C66-C67	108.2(8)
C37-C41-C43	114.5(7)	C62-C66-C67	111.5(7)
C42-C41-C43	110.9(7)	C82-C81-C83	109.3(8)
C45-C44-C49	116.8(7)	C85-C84-C80	112.5(8)
C45-C44-W2	119.3(5)	C85-C84-C86	109.1(8)
C49-C44-W2	123.6(6)	C80-C84-C86	112.3(8)
C46-C45-C44	121.8(7)	C71-C70-W2	142.0(6)
C46-C45-C50	115.2(7)	C53-C52-C56	121.1(7)
C59-C56-C58	105.9(7)	C51-C52-C56	124.2(7)
C52-C56-C58	109.0(7)	C52-C53-C54	123.2(8)
C57-C56-C58	108.4(7)	C55-C54-C53	119.8(8)
C65-C60-C61	115.0(8)	C54-C55-C50	120.6(8)
C65-C60-C49	122.0(8)	C59-C56-C52	113.5(7)
C61-C60-C49	122.9(7)	C59-C56-C57	107.6(8)
O5-C61-C62	118.8(7)	C52-C56-C57	112.2(7)
O5-C61-C60	116.1(7)	C72-C71-C70	109.5(7)
C62-C61-C60	125.1(7)	C72-C71-C73	109.9(8)
C61-C62-C63	116.5(8)	C70-C71-C73	106.8(7)
C61-C62-C66	122.6(7)	C72-C71-C74	110.5(8)
C63-C62-C66	120.8(8)	C70-C71-C74	110.8(6)
C64-C63-C62	120.2(9)	C73-C71-C74	109.2(8)
C63-C64-C65	122.5(8)	O6-C75-C76	119.3(8)
C64-C65-C60	120.6(8)	O6-C75-C80	118.7(8)
C68-C66-C69	109.9(8)	C76-C75-C80	121.9(8)
C68-C66-C62	109.7(8)	C75-C76-C77	118.5(9)
C69-C66-C62	111.0(7)	C75-C76-C81	119.7(8)
C68-C66-C67	106.4(8)	C77-C76-C81	121.8(8)

Table B-4: Continued

Bond	Angle	Bond	Angle
C78-C77-C76	119.7(9)		
C77-C78-C79	121.8(10)		
C78-C79-C80	120.4(10)		
C79-C80-C75	117.5(8)		
C79-C80-C84	120.1(9)		
C75-C80-C84	122.3(8)		
C76-C81-C82	115.7(9)		
C76-C81-C83	107.1(8)		

Table B-5: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for [^{t}BuOCO]W(=CHC(CH$_3$)$_3$)(O-2,6-^{i}Pr$_2$-C$_6$H$_3$) (**3**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

Atom	**U^{11}**	**U^{22}**	**U^{33}**	**U^{23}**	**U^{13}**	**U^{12}**
W1	28(1)	34(1)	23(1)	0(1)	-2(1)	3(1)
W2	24(1)	35(1)	22(1)	-3(1)	2(1)	3(1)
O1	31(3)	35(3)	33(3)	3(3)	-4(3)	6(2)
O2	15(3)	48(3)	30(3)	4(3)	-5(2)	0(2)
O3	28(3)	37(3)	41(3)	-2(3)	-5(3)	2(2)
O4	31(3)	33(3)	30(3)	3(2)	5(3)	2(2)
O5	27(3)	41(3)	27(3)	-5(3)	3(2)	-5(2)
O6	29(3)	47(3)	30(3)	-5(3)	-4(2)	10(3)
C1	27(5)	40(5)	28(5)	-6(4)	9(4)	5(4)
C2	20(4)	45(5)	29(5)	-6(4)	-4(4)	3(4)
C3	43(6)	50(6)	32(5)	-3(4)	-3(4)	6(4)
C4	47(6)	66(7)	26(5)	4(5)	-7(4)	26(5)
C5	34(5)	63(6)	30(5)	-10(4)	-5(4)	17(4)
C6	28(5)	44(5)	28(4)	-3(4)	5(3)	19(4)
C7	28(5)	49(5)	32(5)	7(4)	4(4)	17(4)
C8	22(5)	38(5)	35(5)	5(4)	10(4)	4(4)
C9	46(6)	44(5)	37(5)	2(4)	6(4)	-1(4)
C10	49(6)	48(6)	57(7)	7(5)	5(5)	0(5)
C11	65(7)	42(6)	65(7)	22(5)	7(6)	18(5)
C12	57(7)	47(6)	45(6)	6(5)	0(5)	5(5)
C13	41(6)	44(6)	60(7)	6(5)	-12(5)	6(5)
C14	58(8)	85(9)	137(12)	50(8)	-30(8)	-26(7)
C15	65(8)	65(7)	52(7)	-7(5)	-27(6)	-4(5)
C16	28(6)	108(9)	74(8)	19(7)	-7(6)	-3(6)
C17	42(6)	45(5)	33(5)	-19(4)	11(4)	4(4)
C18	33(5)	43(5)	27(5)	-9(4)	2(4)	10(4)

Table B-5: Continued

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C19	35(5)	50(5)	25(5)	-2(4)	7(4)	6(4)
C20	31(5)	56(6)	47(6)	-15(5)	18(4)	-30(5)
C21	29(5)	72(7)	48(6)	-17(5)	6(5)	-9(5)
C22	19(5)	76(7)	46(6)	-23(5)	2(4)	-8(4)
C23	44(6)	37(5)	55(7)	0(5)	18(5)	-7(4)
C24	81(8)	43(6)	74(8)	5(5)	3(6)	-12(5)
C25	65(7)	41(6)	53(7)	6(5)	-10(5)	8(5)
C26	57(7)	37(5)	72(8)	-4(5)	19(6)	6(5)
C27	23(5)	49(5)	37(5)	1(4)	-14(4)	18(4)
C28	40(6)	41(5)	42(6)	-11(4)	5(4)	3(4)
C29	64(8)	70(8)	107(10)	-39(7)	44(7)	-15(6)
C30	96(9)	63(7)	34(6)	-20(5)	5(6)	1(6)
C31	64(7)	46(6)	46(6)	-10(5)	9(5)	16(5)
C32	21(5)	34(5)	44(5)	2(4)	11(4)	-5(4)
C33	15(4)	47(5)	41(5)	-4(4)	-8(4)	-8(4)
C34	26(5)	63(6)	46(6)	14(5)	-4(4)	16(4)
C35	45(6)	37(5)	52(6)	17(5)	10(5)	10(4)
C36	37(6)	35(5)	46(6)	3(4)	6(4)	-7(4)
C37	10(4)	54(6)	42(5)	14(4)	0(4)	3(4)
C38	20(4)	63(6)	39(5)	2(4)	-15(4)	4(4)
C39	94(10)	69(8)	85(9)	-12(7)	-6(7)	-16(7)
C40	82(8)	75(8)	50(7)	-10(6)	24(6)	-7(6)
C41	19(4)	42(5)	42(5)	-1(4)	-10(4)	9(4)
C42	47(6)	45(5)	42(6)	-1(4)	-1(4)	-11(4)
C43	52(7)	51(6)	51(6)	-4(5)	8(5)	4(5)
C44	37(5)	32(4)	22(4)	0(4)	-3(3)	4(4)
C45	28(5)	41(5)	22(4)	5(4)	3(3)	5(4)

Table B-5: Continued

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C46	38(5)	56(6)	29(5)	3(4)	-1(4)	2(4)
C47	35(5)	77(7)	24(5)	-1(5)	3(4)	9(5)
C48	41(6)	40(5)	39(5)	-15(4)	7(4)	-12(4)
C49	23(5)	47(5)	27(5)	-8(4)	-2(4)	-6(4)
C50	25(5)	38(5)	24(4)	5(4)	-5(4)	-1(4)
C51	30(5)	31(5)	29(5)	6(4)	5(4)	3(4)
C52	27(5)	36(5)	28(5)	3(4)	0(4)	6(4)
C53	42(6)	41(5)	35(5)	3(4)	5(4)	-1(4)
C54	20(5)	58(6)	42(6)	11(5)	-9(4)	5(4)
C55	41(6)	43(5)	31(5)	2(4)	10(4)	7(4)
C56	28(5)	46(5)	39(5)	-8(4)	-11(4)	8(4)
C57	35(6)	60(6)	35(5)	-5(4)	0(4)	1(4)
C58	38(6)	45(5)	57(7)	-1(5)	3(5)	17(4)
C59	41(6)	58(6)	72(7)	-22(5)	-2(5)	9(5)
C60	36(5)	41(5)	23(5)	-4(4)	3(4)	10(4)
C61	15(4)	34(5)	37(5)	-3(4)	-14(4)	6(3)
C62	31(5)	44(5)	31(5)	0(4)	5(4)	16(4)
C63	35(5)	56(6)	34(5)	-4(4)	4(4)	2(4)
C64	43(6)	26(5)	47(6)	-2(4)	-9(5)	8(4)
C65	36(5)	48(6)	37(5)	-4(4)	6(4)	16(4)
C66	30(5)	44(5)	58(7)	-11(5)	10(5)	-12(4)
C67	49(7)	66(7)	96(9)	-20(6)	29(6)	-13(5)
C68	28(6)	64(7)	75(8)	-11(6)	4(5)	-5(5)
C69	43(6)	59(6)	43(6)	-2(5)	16(5)	0(5)
C70	40(5)	27(5)	32(5)	1(3)	6(4)	7(4)
C71	34(5)	44(5)	32(5)	9(4)	-10(4)	0(4)
C72	130(11)	58(7)	39(6)	8(5)	-23(7)	28(7)

Table B-5: Continued

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C73	21(5)	67(7)	109(10)	19(6)	-7(6)	4(5)
C74	53(6)	43(5)	63(7)	17(5)	-28(5)	9(5)
C75	28(5)	32(5)	53(6)	-11(4)	2(4)	8(4)
C76	32(5)	52(6)	34(5)	-8(4)	1(4)	4(4)
C77	34(6)	63(7)	63(7)	1(5)	3(5)	15(5)
C78	56(7)	68(8)	72(9)	-22(6)	12(6)	15(6)
C79	47(7)	71(7)	45(6)	-16(5)	15(5)	10(5)
C80	28(5)	59(6)	33(5)	-10(4)	-2(4)	-5(4)
C81	31(6)	77(7)	49(6)	-8(5)	-11(5)	-3(5)
C82	57(8)	124(10)	49(7)	25(7)	-3(6)	33(7)
C83	79(9)	130(11)	41(7)	-21(7)	-9(6)	-15(8)
C84	45(6)	69(7)	36(5)	-4(5)	5(4)	2(5)
C85	83(9)	90(9)	67(8)	16(7)	-10(7)	-30(7)
C86	83(9)	86(8)	71(8)	16(7)	-5(7)	-29(7)

Table B-6: Torsion angles (in deg) for [^{t}BuOCO]W(=CHC(CH$_3$)$_3$)(O-2,6-^{i}Pr$_2$-C$_6$H$_3$) (**3**)

Atoms	Angle	Atoms	Angle
O2-W1-O1-C8	-51.0(13)	O1-W1-C1-C2	-10.8(6)
C27-W1-O1-C8	101.7(10)	O2-W1-C1-C2	154.8(6)
O3-W1-O1-C8	-35.5(10)	C27-W1-C1-C2	-111.7(6)
C1-W1-O1-C8	2.9(10)	O3-W1-C1-C2	75.6(7)
O1-W1-O2-C18	100.3(9)	C6-C1-C2-C3	8.1(11)
C27-W1-O2-C18	-52.9(7)	W1-C1-C2-C3	-159.8(6)
O3-W1-O2-C18	-174.4(7)	C6-C1-C2-C7	-172.1(7)
C1-W1-O2-C18	46.5(7)	W1-C1-C2-C7	20.0(11)
O1-W1-O3-C32	-59.3(11)	C1-C2-C3-C4	-4.2(12)
O2-W1-O3-C32	38.6(11)	C7-C2-C3-C4	176.0(8)
C27-W1-O3-C32	-54.3(12)	C2-C3-C4-C5	-2.3(13)
C1-W1-O3-C32	117.3(11)	C3-C4-C5-C6	4.9(13)
O5-W2-O4-C51	-110.9(8)	C4-C5-C6-C1	-0.7(12)
C70-W2-O4-C51	38.8(6)	C4-C5-C6-C17	178.9(7)
O6-W2-O4-C51	161.9(6)	C2-C1-C6-C5	-5.8(11)
C44-W2-O4-C51	-56.6(6)	W1-C1-C6-C5	162.2(6)
C70-W2-O5-C61	-108.4(9)	C2-C1-C6-C17	174.7(7)
O4-W2-O5-C61	40.3(13)	W1-C1-C6-C17	-17.4(10)
O6-W2-O5-C61	126.4(8)	C3-C2-C7-C8	162.0(8)
C44-W2-O5-C61	-14.1(8)	C1-C2-C7-C8	-17.8(13)
O5-W2-O6-C75	162.9(11)	C3-C2-C7-C12	-17.0(12)
C70-W2-O6-C75	54.5(12)	C1-C2-C7-C12	163.2(8)
O4-W2-O6-C75	-36.1(11)	W1-O1-C8-C9	178.8(7)
C44-W2-O6-C75	-13.6(11)	W1-O1-C8-C7	-1.3(14)
O1-W1-C1-C6	-178.3(6)	C12-C7-C8-O1	-174.2(7)
O2-W1-C1-C6	-12.8(6)	C2-C7-C8-O1	6.7(11)
C27-W1-C1-C6	80.8(7)	C12-C7-C8-C9	5.7(13)
O3-W1-C1-C6	-92.0(7)	C2-C7-C8-C9	-173.4(8)

Table B-6: Continued

Atoms	Angle	Atoms	Angle
O1-C8-C9-C10	175.1(8)	C17-C18-C19-C23	-175.6(8)
C7-C8-C9-C10	-4.8(14)	C18-C19-C20-C21	-1.1(12)
O1-C8-C9-C13	-7.8(13)	C23-C19-C20-C21	178.5(8)
C7-C8-C9-C13	172.4(9)	C19-C20-C21-C22	-1.5(14)
C8-C9-C10-C11	-0.8(14)	C20-C21-C22-C17	1.3(14)
C13-C9-C10-C11	-178.0(9)	C18-C17-C22-C21	1.3(12)
C9-C10-C11-C12	5.2(16)	C6-C17-C22-C21	-175.4(8)
C10-C11-C12-C7	-4.2(16)	C20-C19-C23-C26	-118.8(9)
C8-C7-C12-C11	-1.0(14)	C18-C19-C23-C26	60.8(10)
C2-C7-C12-C11	178.1(9)	C20-C19-C23-C24	0.9(12)
C8-C9-C13-C16	-57.4(12)	C18-C19-C23-C24	-179.5(8)
C10-C9-C13-C16	119.6(10)	C20-C19-C23-C25	120.0(9)
C8-C9-C13-C15	65.5(11)	C18-C19-C23-C25	-60.4(11)
C10-C9-C13-C15	-17.5(10)	O1-W1-C27-C28	-3.6(9)
C8-C9-C13-C14	-175.2(9)	O2-W1-C27-C28	168.3(8)
C10-C9-C13-C14	1.8(14)	O3-W1-C27-C28	-103.2(8)
C5-C6-C17-C18	-147.1(8)	C1-W1-C27-C28	82.4(9)
C1-C6-C17-C18	32.5(12)	W1-C27-C28-C29	-148.6(8)
C5-C6-C17-C22	29.5(11)	W1-C27-C28-C31	-28.2(12)
C1-C6-C17-C22	-150.9(8)	W1-C27-C28-C30	93.7(10)
W1-O2-C18-C17	-44.0(10)	W1-O3-C32-C33	81.1(12)
W1-O2-C18-C19	138.6(6)	W1-O3-C32-C37	-00.5(12)
C22-C17-C18-O2	178.6(7)	O3-C32-C33-C34	-179.3(7)
C6-C17-C18-O2	-4.7(11)	C37-C32-C33-C34	2.4(12)
C22-C17-C18-C19	-4.1(12)	O3-C32-C33-C38	3.5(12)
C6-C17-C18-C19	172.7(7)	C37-C32-C33-C38	-174.8(7)
O2-C18-C19-C20	-178.8(7)	C32-C33-C34-C35	0.9(13)

Table B-6: Continued

Atoms	Angle	Atoms	Angle
C17-C18-C19-C20	4.0(12)	C38-C33-C34-C35	178.2(8)
O2-C18-C19-C23	1.6(12)	C33-C34-C35-C36	-3.1(14)
C34-C35-C36-C37	1.8(14)	C45-C46-C47-C48	-4.3(12)
C35-C36-C37-C32	1.5(12)	C46-C47-C48-C49	1.6(13)
C35-C36-C37-C41	-174.6(8)	C47-C48-C49-C44	5.2(13)
O3-C32-C37-C36	178.1(7)	C47-C48-C49-C60	-177.1(8)
C33-C32-C37-C36	-3.5(11)	C45-C44-C49-C48	-9.1(11)
O3-C32-C37-C41	-5.7(11)	W2-C44-C49-C48	165.1(6)
C33-C32-C37-C41	172.7(7)	C45-C44-C49-C60	173.5(7)
C34-C33-C38-C39	-67.2(11)	W2-C44-C49-C60	-12.3(11)
C32-C33-C38-C39	110.0(9)	C46-C45-C50-C51	145.9(8)
C34-C33-C38-C40	59.2(10)	C44-C45-C50-C51	-35.3(11)
C32-C33-C38-C40	-123.6(9)	C46-C45-C50-C55	-33.5(10)
C36-C37-C41-C42	100.8(9)	C44-C45-C50-C55	145.2(8)
C32-C37-C41-C42	-75.2(9)	W2-O4-C51-C50	51.1(9)
C36-C37-C41-C43	-26.0(11)	W2-O4-C51-C52	-130.2(6)
C32-C37-C41-C43	158.0(7)	C55-C50-C51-O4	-176.6(6)
O5-W2-C44-C45	-173.9(6)	C45-C50-C51-O4	3.9(11)
C70-W2-C44-C45	-70.6(6)	C55-C50-C51-C52	4.7(11)
O4-W2-C44-C45	21.6(6)	C45-C50-C51-C52	-174.8(7)
O6-W2-C44-C45	99.4(6)	O4-C51-C52-C53	175.5(7)
O5-W2-C44-C49	12.1(6)	C50-C51-C52-C53	-5.9(12)
C70-W2-C44-C49	115.3(6)	O4-C51-C52-C56	-2.9(11)
O4-W2-C44-C49	-152.5(6)	C50-C51-C52-C56	175.7(7)
O6-W2-C44-C49	-74.7(7)	C51-C52-C53-C54	4.5(12)
C49-C44-C45-C46	6.7(11)	C56-C52-C53-C54	-177.0(8)
W2-C44-C45-C46	-167.8(6)	C52-C53-C54-C55	-2.2(13)

Table B-6: Continued

Atoms	Angle	Atoms	Angle
C49-C44-C45-C50	-172.0(7)	C61-C60-C65-C64	3.7(11)
W2-C44-C45-C50	13.6(10)	C49-C60-C65-C64	-179.4(7)
C44-C45-C46-C47	-0.1(12)	C61-C62-C66-C68	56.6(10)
C50-C45-C46-C47	178.6(7)	C63-C62-C66-C68	-118.0(8)
C51-C52-C56-C59	-176.6(8)	C61-C62-C66-C69	-65.1(10)
C53-C52-C56-C57	-117.2(8)	C63-C62-C66-C69	120.3(8)
C51-C52-C56-C57	61.2(10)	C53-C54-C55-C50	0.8(12)
C53-C52-C56-C58	122.8(8)	C51-C50-C55-C54	-1.9(11)
C51-C52-C56-C58	-58.9(10)	C45-C50-C55-C54	177.5(7)
C48-C49-C60-C65	11.5(11)	C53-C52-C56-C59	5.0(11)
C44-C49-C60-C65	-171.0(7)	C61-C62-C66-C67	174.2(8)
C48-C49-C60-C61	-171.9(7)	C63-C62-C66-C67	-0.4(12)
C44-C49-C60-C61	5.7(12)	O5-W2-C70-C71	21.1(10)
W2-O5-C61-C62	-170.1(6)	O4-W2-C70-C71	-49.2(10)
W2-O5-C61-C60	11.1(12)	O6-W2-C70-C71	123.7(9)
C65-C60-C61-O5	174.5(6)	C44-W2-C70-C71	-63.9(10)
C49-C60-C61-O5	-2.4(11)	W2-C70-C71-C72	-138.9(9)
C65-C60-C61-C62	-4.3(11)	W2-C70-C71-C73	102.1(10)
C49-C60-C61-C62	178.9(7)	W2-C70-C71-C74	-16.7(13)
O5-C61-C62-C63	-176.3(7)	W2-O6-C75-C76	95.7(12)
C60-C61-C62-C63	2.4(12)	W2-O6-C75-C80	-87.4(13)
O5-C61-C62-C66	8.8(11)	O6-C75-C76-C77	-178.2(8)
C60-C61-C62-C66	-172.4(8)	C80-C75-C76-C77	5.0(13)
C61-C62-C63-C64	0.1(12)	O6-C75-C76-C81	5.1(12)
C66-C62-C63-C64	175.1(8)	C80-C75-C76-C81	-171.7(8)
C62-C63-C64-C65	-0.5(13)	C75-C76-C77-C78	-2.1(14)
C63-C64-C65-C60	-1.5(13)	C81-C76-C77-C78	174.6(9)

Table B-6: Continued

Atoms	Angle	Atoms	Angle
C76-C77-C78-C79	-1.3(16)		
C77-C78-C79-C80	2.0(16)		
C78-C79-C80-C75	0.9(14)		
C78-C79-C80-C84	-176.4(9)		
O6-C75-C80-C79	178.8(8)		
C76-C75-C80-C79	-4.4(13)		
C79-C80-C84-C85	-63.6(12)		
C75-C80-C84-C85	119.2(10)		
C79-C80-C84-C86	60.0(11)		
C75-C80-C84-C86	-17.2(10)		
O6-C75-C80-C84	-4.0(12)		
C76-C75-C80-C84	172.8(8)		
C75-C76-C81-C82	-161.2(8)		
C77-C76-C81-C82	22.2(13)		
C75-C76-C81-C83	76.6(11)		
C77-C76-C81-C83	-00.0(11)		

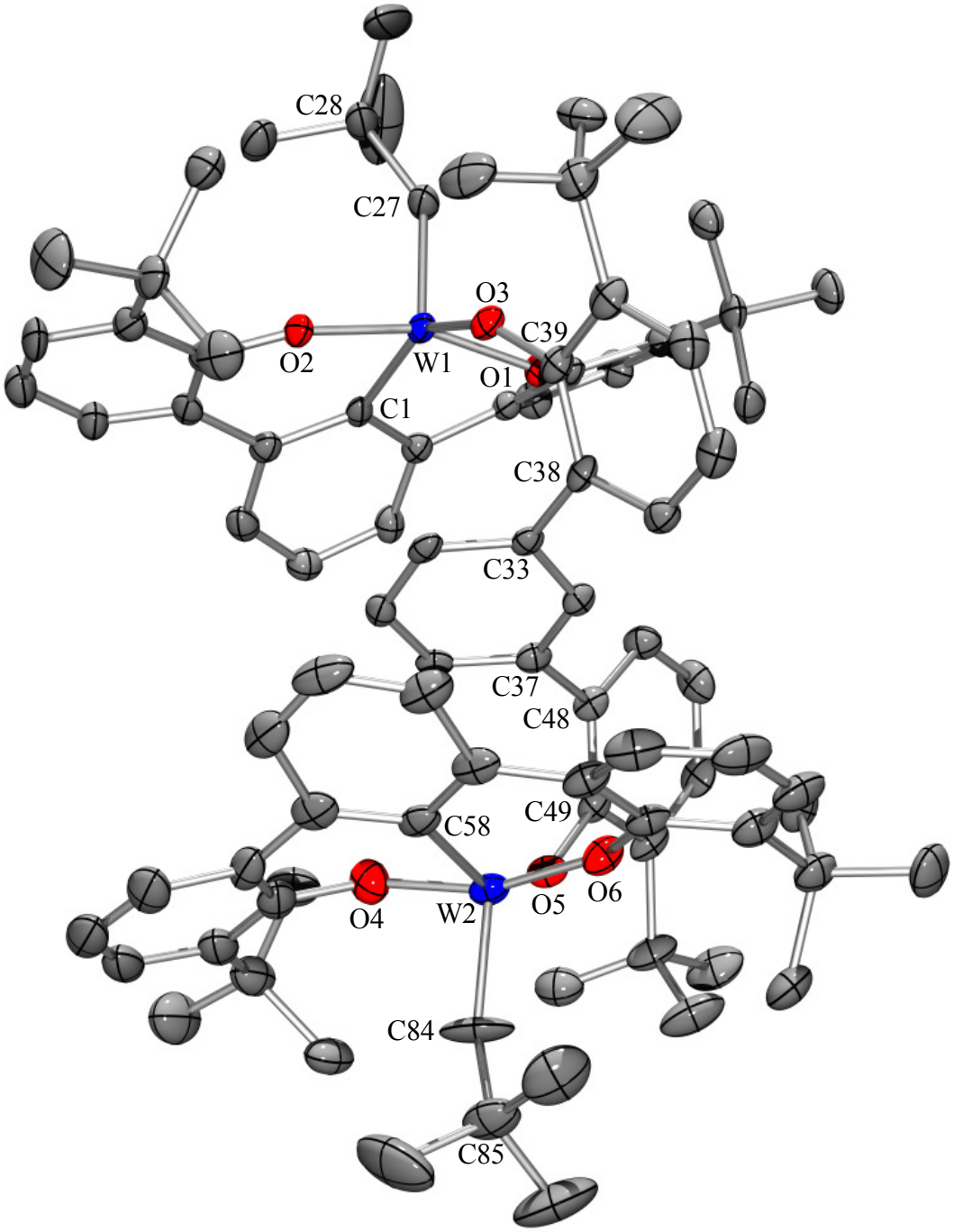


Figure B-3: Molecular structure of {[^{t}BuOCO](CH$_3$)$_3$CCH=}W(μ-^{t}BuOCHO)W{=CHC(CH$_3$)$_3$-[^{t}BuOCO]} (**4**). Ellipsoids are shown at the 50% probability level; hydrogens are omitted for clarity.

X-ray Experimental for {[^{t}BuOCO](CH$_3$)$_3$CCH=}W(μ-^{t}BuOCHO)W{=CHC(CH$_3$)$_3$-[^{t}BuOCO]} (4)

Data were collected at 173 K on a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing MoKα radiation (λ = 0.71073 Å). Cell parameters were refined using up to 8192 reflections. A full sphere of data (1850 frames) was collected using the ω-scan method (0.3°frame width). The first 50 frames were re-measured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was < 1 %). Absorption corrections by integration were applied based on measured indexed crystal faces.

The structure was solved by the author using Direct Methods in *SHELXTL6,* and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. A total of 865 parameters were refined in the final cycle of refinement using 9733 reflections (with I > 2σI) to yield R_1 and wR_2 of 4.58% and 8.68%, respectively. Refinement was done using F^2.

Table B-7: Crystal data, structure solution, and refinement for {[^{t}BuOCO](CH$_3$)$_3$CCH=}W(μ-^{t}BuOCHO)W{=CHC(CH$_3$)$_3$[^{t}BuOCO]} (**4**)

identification code	pelo6t
empirical formula	$C_{88}H_{102}O_6W_2$
formula weight	1623.40
T (K)	173(2)
λ (Å)	0.71073
crystal system	Monoclinic
space group	P2(1)/n
a (Å)	13.5918(11)
b (Å)	35.213(3)
c (Å)	17.2146(15)
α (deg)	90
β (deg)	111.897(2)
γ (deg)	90
V (Å^3)	7644.7(11)
Z	4
ρ_{calcd} (g mm^{-3})	1.411
crystal size (mm)	0.15 x 0.15 x 0.02
abs coeff (mm^{-1})	3.059
F(000)	3304
θ range for data collection	1.16 to 28.06
limiting indicies	$-17 \le h \le 17$, $-32 \le k \le 46$, $-19 \le l \le 22$
no. of reflns collcd	53602
no. of ind reflns	18421 [R(int) = 0.08431]
completeness to *θ*= 28.03°	99.3 %
absorption corr	Integration
refinement method	Full-matrix least-squares on F^2
data / restraints / parameters	18421 / 0 / 865
*R*1, *wR*2 [I > 2σ]	R1 = 0.0458, wR2 = 0.0868
*R*1, *wR*2 (all data)	R1 = 0.1048, wR2 = 0.0967
GOF on F^2	0.845
largest diff. peak and hole (e.Å^{-3})	1.519 and -1.124

$R1 = \Sigma(||F_o| - |F_c||) / \Sigma|F_o|$

$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

$S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$

$w = 1/[\sigma^2(F_o^2)+(m*p)^2+n*p]$, $p = [\max(F_o^2,0)+ 2* F_c^2]/3$, m & n are constants.

Table B-8: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for {[^{t}BuOCO](CH$_3$)$_3$CCH=}W(μ-^{t}BuOCHO)W{=CHC(CH$_3$)$_3$[^{t}BuOCO]} (**4**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	X	Y	Z	U(eq)
W1	2864(1)	1311(1)	883(1)	32(1)
W2	1720(1)	1073(1)	4751(1)	40(1)
O1	3232(3)	809(1)	885(2)	37(1)
O2	2535(3)	1791(1)	1227(2)	31(1)
O3	1339(3)	1219(1)	382(2)	37(1)
O4	3049(3)	847(1)	5077(3)	58(1)
O5	2431(3)	1568(1)	5061(2)	41(1)
O6	453(3)	1293(1)	4124(2)	48(1)
C1	4315(4)	1350(2)	1970(3)	32(1)
C2	4928(4)	1023(2)	2350(4)	36(1)
C3	5632(5)	1049(2)	3184(4)	45(2)
C4	5760(5)	1374(2)	3649(4)	44(2)
C5	5256(4)	1698(2)	3261(4)	39(2)
C6	4576(4)	1698(2)	2432(4)	33(1)
C7	4878(5)	649(2)	1926(4)	40(2)
C8	3997(5)	540(2)	1230(4)	40(2)
C9	3858(5)	173(2)	858(4)	46(2)
C10	4737(6)	-65(2)	1173(5)	56(2)
C11	5636(6)	48(2)	1818(5)	57(2)
C12	5716(5)	392(2)	2206(4)	49(2)
C13	2817(6)	48(2)	189(4)	54(2)
C14	2842(6)	-384(2)	-35(5)	84(3)
C15	2570(5)	281(2)	-623(4)	59(2)
C16	1905(5)	100(2)	502(4)	64(2)
C17	4162(4)	2072(2)	2063(3)	33(1)
C18	3127(4)	2116(2)	1499(3)	32(1)

Table B-8: Continued

Atom	X	Y	Z	U(eq)
C19	2666(5)	2472(2)	1221(3)	35(1)
C20	3354(5)	2779(2)	1498(4)	44(2)
C21	4401(5)	2740(2)	2016(4)	47(2)
C22	4795(5)	2393(2)	2303(4)	45(2)
C23	1504(5)	2522(2)	666(4)	42(2)
C24	1193(5)	2943(2)	507(4)	60(2)
C25	1220(5)	2336(2)	-175(4)	49(2)
C26	810(5)	2355(2)	1118(4)	51(2)
C27	3403(5)	1530(2)	113(4)	45(2)
C28	4187(6)	1468(2)	-315(5)	64(2)
C29	3578(9)	1491(3)	-1241(6)	172(6)
C30	4747(6)	1097(2)	-95(5)	71(2)
C31	5011(7)	1791(2)	-52(8)	153(6)
C32	1448(4)	1578(2)	2608(3)	32(1)
C33	1250(4)	1295(2)	2012(3)	31(1)
C34	1946(4)	984(2)	2194(4)	35(1)
C35	2806(4)	968(2)	2936(4)	35(1)
C36	3005(4)	1262(2)	3507(3)	35(1)
C37	2323(4)	1573(2)	3345(4)	36(1)
C38	303(4)	1319(2)	1218(3)	33(1)
C39	376(4)	1268(2)	424(4)	36(1)
C40	-532(5)	1280(2)	-326(4)	45(2)
C41	-1507(5)	1356(2)	-252(4)	51(2)
C42	-1576(5)	1419(2)	521(5)	52(2)
C43	-692(5)	1400(2)	1238(4)	43(2)
C44	-481(6)	1202(2)	-1181(4)	57(2)
C45	-94(6)	801(2)	-1187(4)	76(2)

Table B-8: Continued

Atom	X	Y	Z	U(eq)
C46	282(5)	1474(2)	-1393(4)	61(2)
C47	-1558(6)	1245(3)	-1892(5)	97(3)
C48	2564(4)	1913(2)	3903(4)	36(1)
C49	2627(4)	1899(2)	4738(4)	34(1)
C50	2826(4)	2232(2)	5233(4)	44(2)
C51	2949(5)	2564(2)	4858(4)	47(2)
C52	2902(5)	2579(2)	4071(4)	55(2)
C53	2712(5)	2258(2)	3573(4)	44(2)
C54	2913(6)	2219(2)	6153(4)	61(2)
C55	3810(6)	1964(2)	6656(4)	66(2)
C56	3138(6)	2618(2)	6540(5)	87(3)
C57	1865(6)	2091(2)	6220(5)	87(3)
C58	1151(5)	620(2)	3851(4)	47(2)
C59	1828(5)	309(2)	3893(4)	53(2)
C60	1611(6)	67(2)	3165(5)	64(2)
C61	738(7)	135(2)	2462(5)	68(2)
C62	35(6)	412(2)	2442(5)	58(2)
C63	184(5)	655(2)	3125(4)	47(2)
C64	2788(6)	207(2)	4627(5)	55(2)
C65	3404(6)	482(2)	5203(5)	54(2)
C66	4365(6)	413(2)	5890(5)	61(2)
C67	4669(7)	27(3)	5969(5)	77(3)
C68	4087(8)	-259(2)	5426(7)	89(3)
C69	3156(7)	-171(2)	4770(6)	72(2)
C70	5017(6)	721(2)	6487(5)	69(2)
C71	6039(6)	565(3)	7151(5)	101(3)
C72	4384(5)	902(2)	6979(4)	70(2)

Table B-8: Continued

Atom	X	Y	Z	U(eq)
C73	5308(6)	1043(2)	6003(5)	83(3)
C74	-669(5)	928(2)	3028(4)	47(2)
C75	-510(5)	1254(2)	3506(4)	43(2)
C76	-1297(5)	1538(2)	3394(4)	52(2)
C77	-2269(6)	1466(2)	2766(4)	63(2)
C78	-2463(6)	1145(3)	2316(5)	68(2)
C79	-1712(6)	870(2)	2433(4)	63(2)
C80	-1074(5)	1891(2)	3942(4)	55(2)
C81	-829(5)	1788(2)	4860(4)	70(2)
C82	-2057(5)	2161(2)	3682(5)	75(2)
C83	-169(5)	2123(2)	3849(5)	65(2)
C84	1367(7)	859(2)	5611(5)	90(3)
C85	605(7)	681(2)	5914(5)	79(3)
C86	882(10)	285(3)	6169(6)	158(5)
C87	522(9)	927(3)	6628(7)	156(5)
C88	-520(6)	701(3)	5158(6)	108(3)

Table B-9: Bond lengths (in Å) for {[^{t}BuOCO](CH$_3$)$_3$CCH=}W(μ-^{t}BuOCHO) W{=CHC(CH$_3$)$_3$-[^{t}BuOCO]} (**4**)

Bond	Length	Bond	Length
W1-O1	1.838(4)	C8-C9	1.422(8)
W1-O2	1.897(3)	C9-C10	1.394(8)
W1-C27	1.900(6)	C9-C13	1.519(9)
W1-O3	1.952(4)	C10-C11	1.369(9)
W1-C1	2.158(6)	C11-C12	1.365(8)
W2-O6	1.830(4)	C13-C16	1.536(8)
W2-O4	1.859(4)	C13-C15	1.546(9)
W2-C84	1.876(6)	C13-C14	1.573(8)
W2-O5	1.969(4)	C17-C22	1.385(7)
W2-C58	2.155(6)	C17-C18	1.387(7)
O1-C8	1.368(6)	C18-C19	1.403(7)
O2-C18	1.378(6)	C19-C20	1.392(7)
O3-C39	1.348(6)	C19-C23	1.521(8)
O4-C65	1.360(8)	C20-C21	1.376(8)
O5-C49	1.358(6)	C21-C22	1.352(8)
O6-C75	1.351(7)	C23-C25	1.503(8)
C1-C2	1.429(7)	C23-C24	1.539(7)
C1-C6	1.430(7)	C23-C26	1.546(8)
C2-C3	1.401(8)	C27-C28	1.520(8)
C2-C7	1.495(8)	C28-C30	1.489(8)
C3-C4	1.368(8)	C28-C29	1.499(11)
C4-C5	1.370(8)	C28-C31	1.539(11)
C5-C6	1.382(7)	C32-C37	1.377(7)
C6-C17	1.481(7)	C32-C33	1.382(7)
C7-C12	1.392(8)	C33-C34	1.403(7)
C7-C8	1.396(8)	C33-C38	1.490(7)
C34-C35	1.375(7)	C61-C62	1.357(10)

Table B-9: Continued

Bond	Length	Bond	Length
C35-C36	1.385(7)	C62-C63	1.406(9)
C36-C37	1.394(8)	C63-C74	1.469(9)
C37-C48	1.492(8)	C64-C69	1.410(9)
C38-C43	1.395(7)	C64-C65	1.417(9)
C38-C39	1.418(7)	C65-C66	1.418(9)
C39-C40	1.416(8)	C66-C67	1.412(10)
C40-C41	1.403(8)	C66-C70	1.529(10)
C40-C44	1.526(9)	C67-C68	1.399(11)
C41-C42	1.386(9)	C68-C69	1.380(11)
C42-C43	1.367(8)	C70-C71	1.533(9)
C44-C45	1.510(9)	C70-C73	1.543(9)
C44-C47	1.526(9)	C70-C72	1.552(9)
C44-C46	1.551(9)	C74-C75	1.382(8)
C48-C53	1.388(8)	C74-C79	1.420(8)
C48-C49	1.409(8)	C75-C76	1.421(9)
C49-C50	1.414(8)	C76-C77	1.383(8)
C50-C51	1.378(8)	C76-C80	1.524(9)
C50-C54	1.544(9)	C77-C78	1.339(10)
C51-C52	1.332(8)	C78-C79	1.366(9)
C52-C53	1.383(8)	C80-C81	1.533(9)
C54-C55	1.503(9)	C80-C83	1.533(8)
C54-C56	1.534(9)	C80-C82	1.562(8)
C54-C57	1.539(8)	C84-C85	1.465(9)
C58-C59	1.415(9)	C85-C86	1.468(11)
C58-C63	1.442(9)	C85-C87	1.543(11)
C59-C60	1.451(9)	C85-C88	1.598(11)
C59-C64	1.483(9)	C60-C61	1.363(10)

Table B-10: Bond angles (in deg) for {[^{t}BuOCO](CH$_3$)$_3$CCH=}W(μ-^{t}BuOCHO) W{=CHC(CH$_3$)$_3$[^{t}BuOCO]} (**4**)

Bond	Angle	Bond	Angle
O1-W1-O2	162.07(16)	C2-C1-W1	122.3(4)
O1-W1-C27	102.5(2)	C6-C1-W1	119.5(4)
O2-W1-C27	93.1(2)	C3-C2-C1	118.3(5)
O1-W1-O3	94.85(15)	C3-C2-C7	116.6(5)
O2-W1-O3	87.16(14)	C1-C2-C7	125.1(5)
C27-W1-O3	112.4(2)	C4-C3-C2	123.0(6)
O1-W1-C1	84.19(19)	C3-C4-C5	118.6(6)
O2-W1-C1	85.33(18)	C4-C5-C6	121.6(6)
C27-W1-C1	96.5(2)	C5-C6-C1	120.4(5)
O3-W1-C1	150.42(17)	C5-C6-C17	116.3(5)
O6-W2-O4	162.78(18)	C1-C6-C17	123.3(5)
O6-W2-C84	100.0(3)	C12-C7-C8	116.6(6)
O4-W2-C84	95.5(3)	C12-C7-C2	121.4(6)
O6-W2-O5	92.42(17)	C8-C7-C2	122.0(5)
O4-W2-O5	88.53(18)	O1-C8-C7	116.8(5)
C84-W2-O5	112.7(3)	O1-C8-C9	118.8(6)
O6-W2-C58	83.3(2)	C7-C8-C9	124.3(6)
O4-W2-C58	87.1(2)	C10-C9-C8	114.9(6)
C84-W2-C58	98.1(3)	C10-C9-C13	122.8(6)
O5-W2-C58	149.19(18)	C8-C9-C13	122.3(6)
C8-O1-W1	146.1(4)	C11-C10-C9	121.0(6)
C18-O2-W1	132.1(3)	C12-C11-C10	122.6(6)
C39-O3-W1	147.9(3)	C11-C12-C7	120.1(7)
C65-O4-W2	134.4(4)	C9-C13-C16	110.2(5)
C49-O5-W2	143.1(4)	C9-C13-C15	111.1(6)
C75-O6-W2	147.5(4)	C16-C13-C15	108.9(6)
C2-C1-C6	117.0(5)	C9-C13-C14	111.5(6)

Table B-10: Continued

Bond	Angle	Bond	Angle
C16-C13-C14	107.1(6)	C32-C33-C38	120.1(5)
C15-C13-C14	108.0(6)	C34-C33-C38	122.0(5)
C22-C17-C18	118.2(5)	C35-C34-C33	120.6(5)
C22-C17-C6	120.2(5)	C34-C35-C36	120.1(5)
C18-C17-C6	121.5(5)	C35-C36-C37	120.4(5)
O2-C18-C17	117.1(5)	C32-C37-C36	118.4(5)
O2-C18-C19	119.8(5)	C32-C37-C48	119.4(5)
C17-C18-C19	123.1(5)	C36-C37-C48	122.0(5)
C20-C19-C18	114.8(6)	C43-C38-C39	117.8(5)
C20-C19-C23	122.2(5)	C43-C38-C33	120.2(5)
C18-C19-C23	123.0(5)	C39-C38-C33	122.0(5)
C21-C20-C19	123.0(6)	O3-C39-C40	119.2(5)
C22-C21-C20	120.1(6)	O3-C39-C38	119.1(5)
C21-C22-C17	120.7(6)	C40-C39-C38	121.6(5)
C25-C23-C19	112.9(5)	C41-C40-C39	117.1(6)
C25-C23-C24	107.1(5)	C41-C40-C44	120.4(6)
C19-C23-C24	112.0(5)	C39-C40-C44	122.5(6)
C25-C23-C26	109.5(5)	C42-C41-C40	121.4(6)
C19-C23-C26	109.0(5)	C43-C42-C41	120.5(6)
C24-C23-C26	106.1(5)	C42-C43-C38	121.4(6)
C28-C27-W1	143.4(5)	C45-C44-C47	108.6(6)
C30-C28-C29	110.2(7)	C45-C44-C40	108.5(6)
C30-C28-C27	112.7(5)	C47-C44-C40	112.4(6)
C29-C28-C27	107.4(6)	C45-C44-C46	108.2(6)
C30-C28-C31	109.1(7)	C47-C44-C46	106.1(6)
C29-C28-C31	109.1(8)	C40-C44-C46	113.0(5)
C27-C28-C31	108.4(7)	C53-C48-C49	119.0(5)

Table B-10: Continued

Bond	Angle	Bond	Angle
C37-C32-C33	122.4(5)	C53-C48-C37	117.9(6)
C32-C33-C34	117.9(5)	C49-C48-C37	123.0(5)
O5-C49-C48	120.0(5)	C65-C64-C59	122.2(6)
O5-C49-C50	119.1(6)	O4-C65-C64	116.9(7)
C48-C49-C50	120.7(5)	O4-C65-C66	117.2(7)
C51-C50-C49	116.8(6)	C64-C65-C66	125.9(7)
C51-C50-C54	121.9(6)	C65-C66-C67	113.0(8)
C49-C50-C54	121.3(6)	C65-C66-C70	124.2(7)
C52-C51-C50	122.8(6)	C67-C66-C70	122.8(8)
C51-C52-C53	121.7(6)	C68-C67-C66	123.8(8)
C52-C53-C48	118.9(6)	C69-C68-C67	120.2(8)
C55-C54-C56	108.0(6)	C68-C69-C64	120.7(8)
C55-C54-C57	110.9(7)	C66-C70-C71	112.6(7)
C56-C54-C57	106.0(6)	C66-C70-C73	111.0(6)
C55-C54-C50	110.1(6)	C71-C70-C73	108.7(6)
C56-C54-C50	110.3(6)	C66-C70-C72	111.0(6)
C57-C54-C50	111.5(6)	C71-C70-C72	105.8(6)
C59-C58-C63	118.4(6)	C73-C70-C72	107.4(7)
C59-C58-W2	118.9(5)	C75-C74-C79	116.2(6)
C63-C58-W2	121.8(5)	C75-C74-C63	122.4(6)
C58-C59-C60	119.4(7)	C79-C74-C63	121.4(6)
C58-C59-C64	125.5(6)	O6-C75-C74	116.3(6)
C60-C59-C64	115.1(7)	O6-C75-C76	119.6(5)
C61-C60-C59	119.6(7)	C74-C75-C76	124.0(6)
C62-C61-C60	121.3(7)	C77-C76-C75	115.4(6)
C61-C62-C63	122.3(7)	C77-C76-C80	123.0(6)
C62-C63-C58	118.3(7)	C75-C76-C80	121.6(6)

Table B-10: Continued

Bond	Angle	Bond	Angle
C62-C63-C74	116.3(6)		
C58-C63-C74	125.4(6)		
C69-C64-C65	116.4(8)		
C69-C64-C59	121.3(7)		
C76-C80-C83	110.6(5)		
C81-C80-C83	111.1(6)		
C76-C80-C82	111.6(6)		
C81-C80-C82	105.9(5)		
C83-C80-C82	106.4(6)		
C85-C84-W2	151.3(7)		
C86-C85-C84	112.1(8)		
C86-C85-C87	112.5(8)		
C84-C85-C87	108.3(7)		
C86-C85-C88	110.2(8)		
C84-C85-C88	106.3(7)		
C87-C85-C88	107.0(8)		
C78-C77-C76	122.0(7)		
C77-C78-C79	122.5(7)		
C78-C79-C74	119.6(7)		
C76-C80-C81	111.1(6)		

Table B-11: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for {[^{t}BuOCO](CH$_3$)$_3$CCH=}W(μ-^{t}BuOCHO) W{=CHC(CH$_3$)$_3$[^{t}BuOCO]} (**4**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

Atom	**U^{11}**	**U^{22}**	**U^{33}**	**U^{23}**	**U^{13}**	**U^{12}**
W1	41(1)	25(1)	36(1)	-1(1)	21(1)	0(1)
W2	48(1)	41(1)	40(1)	-5(1)	25(1)	-14(1)
O1	48(2)	29(2)	38(2)	-1(2)	22(2)	3(2)
O2	35(2)	21(2)	42(2)	-4(2)	19(2)	-2(2)
O3	48(2)	29(2)	38(2)	-8(2)	22(2)	-2(2)
O4	67(3)	43(3)	61(3)	-4(2)	22(3)	-3(2)
O5	49(3)	42(3)	38(2)	-9(2)	21(2)	-13(2)
O6	46(3)	53(3)	46(3)	-18(2)	19(2)	-10(2)
C1	36(3)	30(3)	43(4)	9(3)	29(3)	4(3)
C2	42(4)	35(4)	40(4)	-2(3)	24(3)	-5(3)
C3	44(4)	47(4)	50(4)	18(3)	26(3)	6(3)
C4	44(4)	51(5)	35(4)	-5(3)	13(3)	-5(3)
C5	39(4)	28(4)	51(4)	3(3)	19(3)	3(3)
C6	34(3)	30(3)	39(4)	-6(3)	20(3)	-6(3)
C7	50(4)	35(4)	48(4)	17(3)	32(3)	7(3)
C8	56(4)	31(4)	45(4)	6(3)	34(3)	7(3)
C9	69(5)	33(4)	46(4)	3(3)	33(4)	4(3)
C10	78(5)	33(4)	69(5)	9(4)	41(4)	23(4)
C11	64(5)	45(5)	73(5)	16(4)	39(4)	18(4)
C12	62(5)	40(4)	55(4)	7(3)	33(4)	11(3)
C13	85(5)	27(4)	61(5)	-4(3)	39(4)	5(4)
C14	121(7)	34(5)	91(6)	-24(4)	34(5)	-3(4)
C15	77(5)	51(5)	55(5)	-4(4)	32(4)	7(4)
C16	76(5)	48(5)	69(5)	-3(4)	28(4)	-16(4)
C17	37(4)	33(4)	32(3)	-2(3)	18(3)	3(3)
C18	44(4)	28(3)	35(3)	-3(3)	26(3)	-2(3)

Table B-11: Continued

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C19	51(4)	23(3)	36(4)	3(3)	22(3)	4(3)
C20	69(5)	23(4)	42(4)	3(3)	24(4)	2(3)
C21	59(5)	30(4)	47(4)	-6(3)	16(4)	-12(3)
C22	44(4)	40(4)	51(4)	-3(3)	19(3)	-10(3)
C23	52(4)	25(3)	52(4)	5(3)	23(3)	11(3)
C24	78(5)	36(4)	61(5)	6(3)	20(4)	16(4)
C25	61(4)	35(4)	47(4)	0(3)	15(3)	3(3)
C26	48(4)	45(4)	69(5)	12(3)	31(4)	15(3)
C27	54(4)	35(4)	55(4)	11(3)	29(3)	10(3)
C28	78(5)	62(5)	74(6)	35(4)	54(5)	40(4)
C29	218(12)	258(15)	94(8)	89(9)	122(9)	169(11)
C30	85(6)	69(5)	85(6)	14(4)	64(5)	15(4)
C31	112(8)	72(7)	335(18)	36(9)	154(10)	-7(6)
C32	27(3)	36(4)	38(4)	-5(3)	17(3)	-7(3)
C33	34(3)	33(3)	35(3)	3(3)	23(3)	-3(3)
C34	47(4)	31(4)	43(4)	-3(3)	34(3)	-8(3)
C35	38(4)	29(4)	45(4)	9(3)	22(3)	0(3)
C36	37(3)	44(4)	29(3)	-2(3)	17(3)	-17(3)
C37	35(3)	42(4)	37(4)	-2(3)	21(3)	-6(3)
C38	38(3)	24(3)	40(3)	-11(3)	21(3)	-3(3)
C39	38(3)	28(3)	46(4)	-8(3)	21(3)	-1(3)
C40	50(4)	35(4)	51(4)	-14(3)	20(3)	-7(3)
C41	42(4)	48(4)	53(4)	-7(3)	7(3)	-4(3)
C42	39(4)	46(4)	71(5)	-7(3)	20(4)	-7(3)
C43	53(4)	35(4)	45(4)	-4(3)	26(3)	-4(3)
C44	70(5)	44(5)	53(5)	-16(3)	18(4)	4(4)
C45	115(7)	62(6)	66(5)	-27(4)	52(5)	-32(5)

Table B-11: Continued

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C46	92(6)	55(5)	36(4)	-1(3)	22(4)	-11(4)
C47	77(6)	148(9)	45(5)	-29(5)	-3(4)	-6(5)
C48	30(3)	40(4)	36(4)	-13(3)	11(3)	-10(3)
C49	32(3)	32(4)	43(4)	-3(3)	21(3)	-8(3)
C50	35(4)	52(4)	50(4)	-18(3)	23(3)	-14(3)
C51	60(4)	30(4)	49(4)	-18(3)	19(3)	-7(3)
C52	62(5)	33(4)	61(5)	0(3)	13(4)	-10(3)
C53	51(4)	38(4)	45(4)	1(3)	22(3)	-11(3)
C54	70(5)	74(6)	49(5)	-29(4)	34(4)	-28(4)
C55	85(6)	64(5)	52(5)	-10(4)	28(4)	-21(4)
C56	110(7)	90(7)	72(6)	-50(5)	47(5)	-37(5)
C57	86(6)	115(7)	84(6)	-45(5)	61(5)	-49(5)
C58	73(5)	34(4)	56(5)	-1(3)	48(4)	-9(3)
C59	61(5)	47(5)	64(5)	2(4)	38(4)	-23(4)
C60	93(6)	34(4)	88(6)	-14(4)	61(5)	-22(4)
C61	97(6)	68(6)	56(5)	-32(4)	47(5)	-48(5)
C62	65(5)	55(5)	69(5)	-19(4)	41(4)	-28(4)
C63	66(5)	39(4)	47(4)	-9(3)	32(4)	-34(3)
C64	73(5)	30(4)	87(6)	8(4)	57(5)	1(4)
C65	56(5)	57(5)	64(5)	7(4)	41(4)	-3(4)
C66	69(5)	63(5)	72(6)	26(4)	49(5)	13(4)
C67	87(6)	92(7)	79(6)	38(5)	61(5)	29(6)
C68	140(9)	52(6)	115(8)	29(6)	96(8)	18(6)
C69	91(6)	49(5)	98(7)	16(5)	62(6)	-2(4)
C70	54(5)	92(7)	61(5)	11(5)	20(4)	4(4)
C71	69(6)	143(9)	89(7)	19(6)	29(5)	15(6)
C72	68(5)	98(7)	46(5)	11(4)	23(4)	-5(4)

Table B-11: Continued

Atom	**U^{11}**	**U^{22}**	**U^{33}**	**U^{23}**	**U^{13}**	**U^{12}**
C73	87(6)	95(7)	76(6)	8(5)	42(5)	-31(5)
C74	44(4)	56(5)	51(4)	-10(3)	30(3)	-15(3)
C75	46(4)	54(5)	37(4)	-12(3)	26(3)	-18(3)
C76	41(4)	69(5)	51(4)	-8(4)	25(3)	-9(4)
C77	56(5)	92(6)	52(5)	-19(4)	34(4)	-11(4)
C78	39(4)	119(8)	57(5)	-2(5)	29(4)	-15(5)
C79	69(5)	76(6)	50(5)	-22(4)	30(4)	-47(5)
C80	47(4)	69(5)	57(5)	-7(4)	31(4)	-4(4)
C81	77(5)	79(6)	71(6)	-13(4)	48(5)	1(4)
C82	47(4)	86(6)	107(7)	7(5)	45(5)	14(4)
C83	44(4)	71(6)	84(6)	-5(4)	29(4)	-2(4)
C84	119(7)	126(8)	46(5)	-15(5)	55(5)	-72(6)
C85	111(7)	64(6)	84(6)	-1(5)	63(6)	-26(5)
C86	292(16)	83(8)	99(9)	25(7)	73(10)	-40(9)
C87	204(12)	205(13)	115(9)	-48(8)	125(9)	-47(10)
C88	92(7)	123(9)	127(9)	-23(7)	63(7)	-46(6)

Table B-12: Torsion angles (in deg) for {[^{t}BuOCO](CH$_3$)$_3$CCH=}W(μ-^{t}BuOCHO) W-{=CHC(CH$_3$)$_3$[^{t}BuOCO]} (**4**)

Atoms	Angle	Atoms	Angle
O2-W1-O1-C8	-62.5(9)	O3-W1-C1-C2	82.5(5)
C27-W1-O1-C8	87.4(6)	O1-W1-C1-C6	-174.4(4)
O3-W1-O1-C8	-158.3(6)	O2-W1-C1-C6	-9.0(4)
C1-W1-O1-C8	-8.0(6)	C27-W1-C1-C6	83.7(4)
O1-W1-O2-C18	99.5(6)	O3-W1-C1-C6	-84.8(5)
C27-W1-O2-C18	-51.2(5)	C6-C1-C2-C3	8.9(7)
O3-W1-O2-C18	-163.5(5)	W1-C1-C2-C3	-158.8(4)
C1-W1-O2-C18	45.2(4)	C6-C1-C2-C7	-171.5(5)
O1-W1-O3-C39	127.2(7)	W1-C1-C2-C7	20.9(7)
O2-W1-O3-C39	-35.0(7)	C1-C2-C3-C4	-0.3(8)
C27-W1-O3-C39	-127.2(7)	C7-C2-C3-C4	-180.0(5)
C1-W1-O3-C39	40.4(8)	C2-C3-C4-C5	-6.4(9)
O6-W2-O4-C65	-97.3(8)	C3-C4-C5-C6	4.0(9)
C84-W2-O4-C65	56.7(6)	C4-C5-C6-C1	4.9(8)
O5-W2-O4-C65	169.3(6)	C4-C5-C6-C17	-174.3(5)
C58-W2-O4-C65	-41.2(6)	C2-C1-C6-C5	-11.2(8)
O6-W2-O5-C49	-53.9(6)	W1-C1-C6-C5	156.7(4)
O4-W2-O5-C49	108.9(6)	C2-C1-C6-C17	167.9(5)
C84-W2-O5-C49	-155.8(6)	W1-C1-C6-C17	-24.1(7)
C58-W2-O5-C49	27.1(8)	C3-C2-C7-C12	-22.9(8)
O4-W2-O6-C75	66.2(10)	C1-C2-C7-C12	157.4(5)
C84-W2-O6-C75	-87.4(7)	C3-C2-C7-C8	157.5(5)
O5-W2-O6-C75	159.1(7)	C1-C2-C7-C8	-22.1(8)
C58-W2-O6-C75	9.7(7)	W1-O1-C8-C7	8.3(9)
O1-W1-C1-C2	-7.1(4)	W1-O1-C8-C9	-170.9(4)
O2-W1-C1-C2	158.4(4)	C12-C7-C8-O1	-171.7(5)
C27-W1-C1-C2	-109.0(4)	C2-C7-C8-O1	7.9(8)

Table B-12: Continued

Atoms	Angle	Atoms	Angle
C12-C7-C8-C9	7.4(9)	C17-C18-C19-C20	5.1(8)
C2-C7-C8-C9	-173.0(5)	O2-C18-C19-C23	4.0(8)
O1-C8-C9-C10	171.3(5)	C17-C18-C19-C23	-174.3(5)
C7-C8-C9-C10	-7.8(9)	C18-C19-C20-C21	-1.0(8)
O1-C8-C9-C13	-10.5(8)	C23-C19-C20-C21	178.4(6)
C7-C8-C9-C13	170.3(6)	C19-C20-C21-C22	-2.4(10)
C8-C9-C10-C11	2.9(9)	C20-C21-C22-C17	1.8(9)
C13-C9-C10-C11	-175.2(6)	C18-C17-C22-C21	2.2(9)
C9-C10-C11-C12	2.1(11)	C6-C17-C22-C21	-175.3(5)
C10-C11-C12-C7	-2.7(10)	C20-C19-C23-C25	117.5(6)
C8-C7-C12-C11	-1.9(9)	C18-C19-C23-C25	-63.1(7)
C2-C7-C12-C11	178.5(6)	C20-C19-C23-C24	-3.4(8)
C10-C9-C13-C16	123.4(6)	C18-C19-C23-C24	175.9(5)
C8-C9-C13-C16	-54.6(8)	C20-C19-C23-C26	-120.5(6)
C10-C9-C13-C15	-115.9(7)	C18-C19-C23-C26	58.8(7)
C8-C9-C13-C15	66.1(8)	O1-W1-C27-C28	-19.5(9)
C10-C9-C13-C14	4.7(9)	O2-W1-C27-C28	151.6(8)
C8-C9-C13-C14	-173.3(6)	O3-W1-C27-C28	-120.2(8)
C5-C6-C17-C22	35.2(7)	C1-W1-C27-C28	65.9(9)
C1-C6-C17-C22	-144.0(5)	W1-C27-C28-C30	2.7(12)
C5-C6-C17-C18	-142.2(5)	W1-C27-C28-C29	124.2(9)
C1-C6-C17-C18	38.7(8)	W1-C27-C28-C31	-118.1(9)
W1-O2-C18-C17	-43.1(7)	C37-C32-C33-C34	3.3(8)
W1-O2-C18-C19	138.5(4)	C37-C32-C33-C38	-178.6(5)
C22-C17-C18-O2	175.8(5)	C32-C33-C34-C35	-1.2(7)
C6-C17-C18-O2	-6.8(7)	C38-C33-C34-C35	-179.3(5)
C22-C17-C18-C19	-5.8(8)	C33-C34-C35-C36	-1.1(8)

Table B-12: Continued

Atoms	Angle	Atoms	Angle
C6-C17-C18-C19	171.5(5)	C34-C35-C36-C37	1.5(8)
O2-C18-C19-C20	-176.5(5)	C33-C32-C37-C36	-2.9(8)
C33-C32-C37-C48	171.7(5)	C32-C37-C48-C53	-57.8(7)
C35-C36-C37-C32	0.4(8)	C36-C37-C48-C53	116.5(6)
C35-C36-C37-C48	-174.0(5)	C32-C37-C48-C49	120.9(6)
C32-C33-C38-C43	-48.6(7)	C36-C37-C48-C49	-64.8(8)
C34-C33-C38-C43	129.4(5)	W2-O5-C49-C48	-21.6(9)
C32-C33-C38-C39	130.5(5)	W2-O5-C49-C50	154.4(5)
C34-C33-C38-C39	-51.5(8)	C53-C48-C49-O5	176.6(5)
W1-O3-C39-C40	150.8(5)	C37-C48-C49-O5	-2.1(8)
W1-O3-C39-C38	-27.0(9)	C53-C48-C49-C50	0.6(8)
C43-C38-C39-O3	175.0(5)	C37-C48-C49-C50	-178.0(5)
C33-C38-C39-O3	-4.2(8)	O5-C49-C50-C51	-175.7(5)
C43-C38-C39-C40	-2.8(8)	C48-C49-C50-C51	0.2(8)
C33-C38-C39-C40	178.0(5)	O5-C49-C50-C54	4.9(8)
O3-C39-C40-C41	-176.0(5)	C48-C49-C50-C54	-179.1(6)
C38-C39-C40-C41	1.8(9)	C49-C50-C51-C52	-1.0(9)
O3-C39-C40-C44	6.0(9)	C54-C50-C51-C52	178.4(6)
C38-C39-C40-C44	-176.2(5)	C50-C51-C52-C53	0.8(11)
C39-C40-C41-C42	0.4(9)	C51-C52-C53-C48	0.1(10)
C44-C40-C41-C42	178.4(6)	C49-C48-C53-C52	-0.8(9)
C40-C41-C42-C43	-1.5(9)	C37-C48-C53-C52	177.9(5)
C41-C42-C43-C38	0.5(9)	C51-C50-C54-C55	-118.7(7)
C39-C38-C43-C42	1.7(8)	C49-C50-C54-C55	60.6(8)
C33-C38-C43-C42	-179.2(5)	C51-C50-C54-C56	0.3(9)
C41-C40-C44-C45	-116.3(7)	C49-C50-C54-C56	179.6(6)
C39-C40-C44-C45	61.7(8)	C51-C50-C54-C57	117.8(7)

Table B-12: Continued

Atoms	Angle	Atoms	Angle
C41-C40-C44-C47	3.8(9)	C49-C50-C54-C57	-62.9(9)
C39-C40-C44-C47	-178.3(6)	O6-W2-C58-C59	175.2(5)
C41-C40-C44-C46	123.8(7)	O4-W2-C58-C59	9.5(5)
C39-C40-C44-C46	-58.2(8)	C84-W2-C58-C59	-85.6(5)
O5-W2-C58-C59	91.7(6)	O4-C65-C66-C67	-180.0(5)
O6-W2-C58-C63	6.3(4)	C64-C65-C66-C67	-1.1(9)
O4-W2-C58-C63	-159.3(5)	O4-C65-C66-C70	-0.1(9)
C84-W2-C58-C63	105.5(5)	C64-C65-C66-C70	178.8(6)
O5-W2-C58-C63	-77.2(6)	C65-C66-C67-C68	0.3(10)
C63-C58-C59-C60	8.6(8)	C70-C66-C67-C68	-179.6(7)
W2-C58-C59-C60	-160.6(4)	C66-C67-C68-C69	-0.4(12)
C63-C58-C59-C64	-173.1(5)	C67-C68-C69-C64	1.2(11)
W2-C58-C59-C64	17.6(8)	C65-C64-C69-C68	-1.9(10)
C58-C59-C60-C61	-2.4(9)	C59-C64-C69-C68	175.9(7)
C64-C59-C60-C61	179.2(6)	C65-C66-C70-C71	-177.9(6)
C59-C60-C61-C62	-3.4(10)	C67-C66-C70-C71	2.0(10)
C60-C61-C62-C63	2.8(11)	C65-C66-C70-C73	-55.8(9)
C61-C62-C63-C58	3.7(9)	C67-C66-C70-C73	124.1(7)
C61-C62-C63-C74	-177.0(6)	C65-C66-C70-C72	63.6(9)
C59-C58-C63-C62	-9.2(8)	C67-C66-C70-C72	-116.5(7)
W2-C58-C63-C62	159.7(4)	C62-C63-C74-C75	-159.2(6)
C59-C58-C63-C74	171.5(5)	C58-C63-C74-C75	20.2(9)
W2-C58-C63-C74	-19.6(8)	C62-C63-C74-C79	20.9(9)
C58-C59-C64-C69	152.9(6)	C58-C63-C74-C79	-159.8(6)
C60-C59-C64-C69	-28.8(8)	W2-O6-C75-C74	-10.9(10)
C58-C59-C64-C65	-29.4(9)	W2-O6-C75-C76	167.6(5)
C60-C59-C64-C65	148.9(6)	C79-C74-C75-O6	174.1(5)

Table B-12: Continued

Atoms	Angle	Atoms	Angle
W2-O4-C65-C64	39.8(8)	C63-C74-C75-O6	-5.8(9)
W2-O4-C65-C66	-141.2(5)	C79-C74-C75-C76	-4.4(9)
C69-C64-C65-O4	-179.2(5)	C63-C74-C75-C76	175.7(6)
C59-C64-C65-O4	3.0(9)	O6-C75-C76-C77	-177.7(5)
C69-C64-C65-C66	1.9(10)	C74-C75-C76-C77	0.7(9)
C59-C64-C65-C66	-175.9(6)	O6-C75-C76-C80	1.5(9)
C74-C75-C76-C80	179.9(6)		
C75-C76-C77-C78	2.3(10)		
C80-C76-C77-C78	-176.9(7)		
C76-C77-C78-C79	-1.4(11)		
C77-C78-C79-C74	-2.6(11)		
C75-C74-C79-C78	5.2(9)		
C63-C74-C79-C78	-174.9(6)		
C77-C76-C80-C81	116.0(7)		
C75-C76-C80-C81	-63.1(8)		
C77-C76-C80-C83	-120.1(7)		
C75-C76-C80-C83	60.8(8)		
C77-C76-C80-C82	-1.9(9)		
C75-C76-C80-C82	179.0(6)		
O6-W2-C84-C85	33.2(15)		
O4-W2-C84-C85	-139.2(14)		
O5-W2-C84-C85	130.1(14)		
C58-W2-C84-C85	-51.4(15)		
W2-C84-C85-C86	113.0(15)		
W2-C84-C85-C87	-122.2(14)		
W2-C84-C85-C88	-7.5(17)		

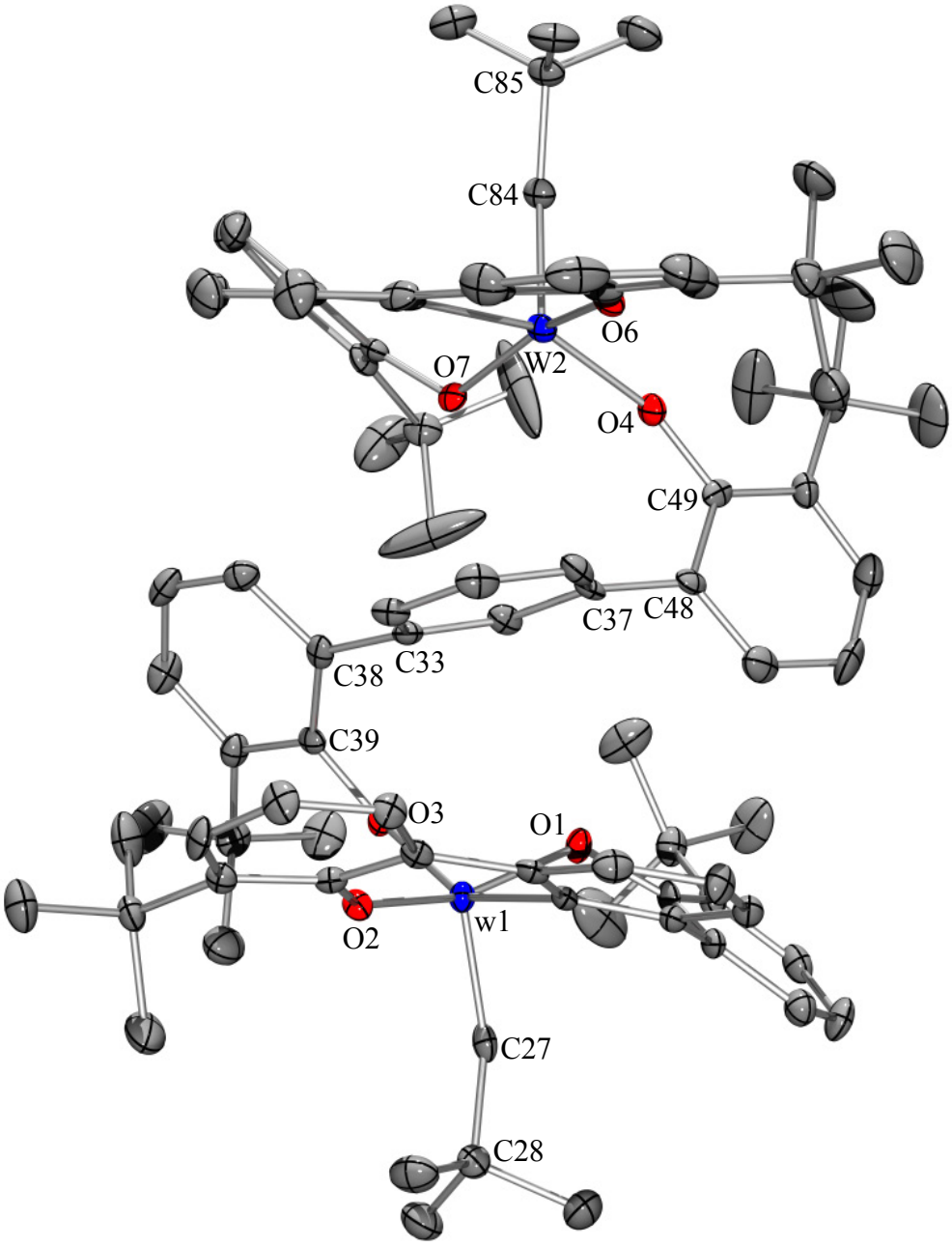


Figure B-4: Molecular structure of {[^{t}BuOCO](CH$_3$)$_3$CCH=}W(μ-^{t}BuOCHO)W{=CHC(CH$_3$)$_3$-[^{t}BuOCO]} (**5**). Ellipsoids are shown at the 50% probability level; hydrogens are omitted for clarity.

X-ray Experimental for {[^{t}BuOCO](CH$_3$)$_3$CCH=}W(μ-^{t}BuOCHO)W{=CHC(CH$_3$)$_3$-[^{t}BuOCO]} (5)

Data were collected at 173 K on a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing MoKα radiation (λ = 0.71073 Å). Cell parameters were refined using up to 8192 reflections. A full sphere of data (1850 frames) was collected using the ω-scan method (0.3°frame width). The first 50 frames were re-measured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was < 1 %). Absorption corrections by integration were applied based on measured indexed crystal faces.

The structure was solved by the author using Direct Methods in *SHELXTL6,* and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. A total of 865 parameters were refined in the final cycle of refinement using 8981 reflections (with I > 2σI) to yield R_1 and wR_2 of 4.85% and 9.19%, respectively. Refinement was done using F^2.

Table B-13: Crystal data, structure solution, and refinement for {[^{t}BuOCO](CH$_3$)$_3$CCH=}W(μ-^{t}BuOCHO)W{=CHC(CH$_3$)$_3$[^{t}BuOCO]} (**5**)

identification code	pelo7t
empirical formula	$C_{88}H_{102}O_6W_2$
formula weight	1623.40
T (K)	173(2)
λ (Å)	0.71073
crystal system	Monoclinic
Space group	P2(1)/c
a (Å)	12.8904(8)
b (Å)	20.2444(13)
c (Å)	29.2372(18)
α (deg)	90
β (deg)	100.7990(10)
ɣ (deg)	90
V (Å^3)	7494.6(8)
Z	4
ρ_{calcd}(g mm^{-3})	1.439
crystal size (mm)	0.16 x 0.04 x 0.04
abs coeff (mm^{-1})	3.121
F(000)	3304
θ range for data collection (deg)	1.23 to 27.50
limiting indices	$-16 \le h \le 15$, $-26 \le k \le 26$, $-37 \le l \le 27$
no. of reflns collcd	50772
no. of ind reflns (R_{int})	17182 (0.1065)
completeness to *θ*= 27.50°	99.8 %
absorption corr	Integration
refinement method	Full-matrix least-squares on F^2
data / restraints / parameters	17182 / 0 / 865
*R*1, *wR*2 [I > 2σ]	0.0485, 0.0919
*R*1, *wR*2 (all data)	0.1179, 0.1030
GOF on F^2	0.849
largest diff. peak and hole (e.Å^{-3})	1.315 and -0.693

$R1 = \Sigma(||F_o| - |F_c||) / \Sigma|F_o|$

$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

$S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$

$w = 1/[\sigma^2(F_o^2)+(m*p)^2+n*p]$, $p = [\max(F_o^2,0)+ 2* F_c^2]/3$, m & n are constants.

Table B-14: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for {[^{t}BuOCO](CH$_3$)$_3$CCH=}W(μ-^{t}BuOCHO)W{=CHC(CH$_3$)$_3$[^{t}BuOCO]} (**5**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	X	Y	Z	U(eq)
W1	2846(1)	5902(1)	3082(1)	23(1)
W2	1520(1)	7759(1)	4941(1)	25(1)
O1	3158(3)	6825(2)	3077(2)	27(1)
O2	2665(3)	5061(2)	3320(2)	24(1)
O3	1352(4)	6134(2)	2974(2)	26(1)
O4	2271(4)	8291(2)	4554(2)	29(1)
O5	462(4)	7588(2)	4407(2)	26(1)
O6	2685(4)	7592(2)	5399(2)	30(1)
C1	4361(5)	5841(3)	3525(2)	23(2)
C2	5149(5)	6305(3)	3458(2)	24(2)
C3	6111(6)	6317(3)	3763(2)	28(2)
C4	6329(5)	5883(4)	4128(2)	31(2)
C5	5606(6)	5423(4)	4193(2)	33(2)
C6	4603(6)	5382(3)	3904(2)	26(2)
C7	5002(6)	6810(3)	3089(2)	25(2)
C8	4009(6)	7100(3)	2937(2)	28(2)
C9	3849(6)	7671(4)	2653(2)	31(2)
C10	4751(6)	7872(4)	2484(3)	36(2)
C11	5719(6)	7557(4)	2592(3)	41(2)
C12	5838(6)	7049(3)	2897(2)	34(2)
C13	2798(6)	8024(4)	2512(3)	37(2)
C14	2196(8)	7689(5)	2083(4)	91(4)
C15	2967(7)	8762(4)	2393(3)	68(3)
C16	2128(7)	8053(4)	2892(3)	61(3)
C17	3891(5)	4840(3)	4002(2)	23(2)
C18	2982(5)	4651(3)	3694(2)	23(2)

Table B-14: Continued

Atom	X	Y	Z	U(eq)
C19	2358(5)	4096(3)	3748(2)	25(2)
C20	2677(6)	3756(3)	4159(3)	33(2)
C21	3528(6)	3946(3)	4489(3)	35(2)
C22	4134(6)	4472(4)	4416(2)	28(2)
C23	1402(6)	3866(3)	3393(2)	29(2)
C24	1695(8)	3729(5)	2928(3)	69(3)
C25	525(6)	4367(4)	3328(3)	53(2)
C26	934(6)	3233(4)	3548(3)	48(2)
C27	3327(5)	5737(3)	2521(2)	29(2)
C28	3869(6)	5225(4)	2265(3)	32(2)
C29	4957(6)	5506(4)	2218(3)	50(2)
C30	3213(7)	5139(4)	1778(3)	53(2)
C31	4011(7)	4586(4)	2521(3)	50(2)
C32	2141(6)	6883(3)	3945(2)	27(2)
C33	1686(6)	6268(3)	3977(2)	25(2)
C34	2131(6)	5841(3)	4343(2)	27(2)
C35	3025(6)	6050(4)	4647(3)	35(2)
C36	3485(6)	6661(3)	4610(2)	30(2)
C37	3046(6)	7085(3)	4260(2)	23(2)
C38	660(5)	6097(3)	3677(3)	26(2)
C39	492(6)	6074(3)	3185(2)	23(2)
C40	-518(5)	5957(3)	2907(2)	29(2)
C41	-1325(6)	5843(4)	3143(3)	40(2)
C42	-1180(6)	5832(4)	3627(3)	38(2)
C43	-220(6)	5965(3)	3882(3)	33(2)
C44	-704(6)	5991(4)	2372(3)	41(2)
C45	-397(7)	6663(4)	2216(3)	56(3)

Table B-14: Continued

Atom	X	Y	Z	U(eq)
C46	-64(7)	5458(4)	2177(3)	55(2)
C47	-1867(6)	5877(5)	2156(3)	72(3)
C48	3520(5)	7738(4)	4189(2)	25(2)
C49	3095(5)	8333(4)	4324(2)	24(2)
C50	3488(6)	8950(3)	4232(2)	30(2)
C51	4339(6)	8947(4)	4011(3)	43(2)
C52	4783(6)	8389(5)	3884(3)	50(2)
C53	4379(6)	7781(4)	3980(3)	40(2)
C54	3044(7)	9595(4)	4378(3)	45(2)
C55	3169(10)	9630(4)	4898(4)	101(4)
C56	1884(7)	9642(4)	4149(4)	95(4)
C57	3606(8)	10197(4)	4237(4)	79(3)
C58	944(6)	6882(3)	5211(2)	26(2)
C59	-137(6)	6711(3)	5045(2)	31(2)
C60	-530(7)	6095(4)	5148(3)	39(2)
C61	105(8)	5640(4)	5422(3)	52(2)
C62	1116(7)	5802(4)	5604(3)	50(2)
C63	1569(6)	6421(4)	5512(2)	34(2)
C64	-896(6)	7145(3)	4755(2)	29(2)
C65	-592(6)	7549(3)	4406(2)	23(2)
C66	-1316(6)	7895(3)	4079(2)	29(2)
C67	-2365(6)	7895(4)	4150(3)	46(2)
C68	-2680(7)	7555(4)	4509(3)	47(2)
C69	-1978(7)	7174(4)	4797(3)	47(2)
C70	-1033(6)	8257(4)	3671(3)	37(2)
C71	-354(12)	7854(7)	3421(4)	181(9)
C72	-449(13)	8858(6)	3826(4)	188(9)

Table B-14: Continued

Atom	X	Y	Z	U(eq)
C73	-1956(8)	8442(6)	3313(3)	91(4)
C74	2683(6)	6545(3)	5755(2)	29(2)
C75	3228(6)	7142(3)	5705(2)	31(2)
C76	4250(6)	7289(4)	5937(3)	38(2)
C77	4745(7)	6809(4)	6231(3)	44(2)
C78	4244(7)	6207(5)	6283(3)	53(3)
C79	3243(7)	6073(4)	6054(3)	46(2)
C80	4807(6)	7943(4)	5880(3)	38(2)
C81	5885(7)	7982(4)	6206(3)	63(3)
C82	4987(7)	8016(4)	5389(3)	48(2)
C83	4151(7)	8518(4)	6006(3)	55(3)
C84	705(6)	8342(3)	5232(2)	28(2)
C85	486(6)	8599(3)	5692(2)	32(2)
C86	1161(7)	8210(4)	6097(3)	49(2)
C87	781(7)	9324(4)	5740(3)	55(3)
C88	-678(6)	8504(4)	5703(3)	51(2)

Table B-15: Bond lengths (in Å) for {[^{t}BuOCO](CH$_3$)$_3$CCH=}W(μ-^{t}BuOCHO)-W{=CHC(CH$_3$)$_3$[^{t}BuOCO]} (**5**)

Bond	Length	Bond	Length
W1-O2	1.870(4)	C8-C9	1.414(9)
W1-C27	1.887(7)	C9-C10	1.407(9)
W1-O1	1.914(4)	C9-C13	1.519(10)
W1-O3	1.950(5)	C10-C11	1.384(10)
W1-C1	2.135(7)	C11-C12	1.351(9)
W2-O6	1.846(5)	C13-C14	1.508(11)
W2-C84	1.885(6)	C13-C16	1.531(10)
W2-O5	1.903(5)	C13-C15	1.558(10)
W2-O4	1.948(4)	C17-C18	1.391(9)
W2-C58	2.131(7)	C17-C22	1.403(9)
O1-C8	1.360(7)	C18-C19	1.406(9)
O2-C18	1.374(7)	C19-C20	1.380(9)
O3-C39	1.371(7)	C19-C23	1.526(10)
O4-C49	1.363(7)	C20-C21	1.372(10)
O5-C65	1.361(8)	C21-C22	1.363(9)
O6-C75	1.373(8)	C23-C25	1.504(10)
C1-C2	1.424(9)	C23-C24	1.505(10)
C1-C6	1.437(9)	C23-C26	1.519(9)
C2-C3	1.385(9)	C27-C28	1.522(9)
C2-C7	1.473(9)	C28-C31	1.489(9)
C3-C4	1.372(9)	C28-C30	1.522(10)
C4-C5	1.356(9)	C28-C29	1.544(10)
C5-C6	1.408(9)	C32-C33	1.388(9)
C6-C17	1.493(9)	C32-C37	1.403(9)
C7-C12	1.393(9)	C33-C34	1.411(9)
C7-C8	1.402(10)	C33-C38	1.484(10)
C34-C35	1.382(10)	C61-C62	1.352(11)

Table B-15: Continued

Bond	Length	Bond	Length
C35-C36	1.383(9)	C60-C61	1.383(11)
C36-C37	1.375(9)	C62-C63	1.430(10)
C37-C48	1.487(9)	C63-C74	1.498(10)
C38-C43	1.404(9)	C64-C65	1.417(9)
C38-C39	1.414(9)	C64-C69	1.425(10)
C39-C40	1.420(9)	C65-C66	1.395(9)
C40-C41	1.373(9)	C66-C67	1.405(10)
C40-C44	1.539(10)	C66-C70	1.501(10)
C41-C42	1.392(10)	C67-C68	1.378(10)
C42-C43	1.345(10)	C68-C69	1.356(11)
C44-C45	1.511(10)	C70-C72	1.458(12)
C44-C46	1.531(10)	C70-C73	1.479(11)
C44-C47	1.531(10)	C70-C71	1.484(11)
C48-C53	1.364(9)	C74-C79	1.401(10)
C48-C49	1.410(9)	C74-C75	1.420(10)
C49-C50	1.392(9)	C75-C76	1.396(10)
C50-C51	1.373(10)	C76-C77	1.373(10)
C50-C54	1.519(10)	C76-C80	1.530(11)
C51-C52	1.350(10)	C77-C78	1.401(11)
C52-C53	1.386(10)	C78-C79	1.365(11)
C54-C55	1.501(12)	C80-C82	1.502(10)
C54-C57	1.514(10)	C80-C83	1.525(10)
C54-C56	1.523(12)	C80-C81	1.532(11)
C58-C63	1.424(9)	C84-C85	1.517(9)
C58-C59	1.429(10)	C85-C87	1.517(10)
C59-C60	1.400(9)	C85-C88	1.520(10)
C59-C64	1.463(10)	C85-C86	1.547(10)

Table B-16: Bond angles (in deg) for {[^{t}BuOCO](CH$_3$)$_3$CCH=}W(μ-^{t}BuOCHO) W{=CHC(CH$_3$)$_3$[^{t}BuOCO]} (**5**)

Bond	Angle	Bond	Angle
O2-W1-C27	104.3(2)	C2-C1-C6	118.4(6)
O2-W1-O1	158.92(19)	C2-C1-W1	118.3(5)
C27-W1-O1	93.6(2)	C6-C1-W1	123.2(5)
O2-W1-O3	95.21(18)	C3-C2-C1	120.0(6)
C27-W1-O3	112.2(2)	C3-C2-C7	115.8(6)
O1-W1-O3	88.04(18)	C1-C2-C7	124.1(6)
O2-W1-C1	83.4(2)	C4-C3-C2	121.2(7)
C27-W1-C1	96.0(3)	C5-C4-C3	120.2(7)
O1-W1-C1	83.7(2)	C4-C5-C6	122.4(7)
O3-W1-C1	151.1(2)	C5-C6-C1	117.8(7)
O6-W2-C84	103.6(3)	C5-C6-C17	117.2(7)
O6-W2-O5	157.29(18)	C1-C6-C17	124.9(6)
C84-W2-O5	96.3(3)	C12-C7-C8	117.2(7)
O6-W2-O4	95.6(2)	C12-C7-C2	122.2(7)
C84-W2-O4	107.1(2)	C8-C7-C2	120.5(6)
O5-W2-O4	88.90(18)	O1-C8-C7	118.2(6)
O6-W2-C58	82.6(2)	O1-C8-C9	118.3(7)
C84-W2-C58	95.4(3)	C7-C8-C9	123.5(6)
O5-W2-C58	84.6(2)	C10-C9-C8	113.8(7)
O4-W2-C58	157.2(2)	C10-C9-C13	121.4(7)
C8-O1-W1	125.7(4)	C8-C9-C13	124.6(7)
C18-O2-W1	143.9(4)	C11-C10-C9	123.7(7)
C39-O3-W1	139.8(4)	C12-C11-C10	119.2(7)
C49-O4-W2	147.1(4)	C11-C12-C7	121.9(8)
C65-O5-W2	125.0(4)	C14-C13-C9	107.9(7)
C75-O6-W2	147.2(5)	C14-C13-C16	110.4(8)
C9-C13-C16	114.6(6)	C33-C32-C37	121.8(7)

Table B-16: Continued

Bond	Angle	Bond	Angle
C14-C13-C15	108.5(7)	C32-C33-C34	118.8(7)
C9-C13-C15	110.9(7)	C32-C33-C38	120.7(6)
C16-C13-C15	104.4(7)	C34-C33-C38	119.8(6)
C18-C17-C22	115.9(6)	C35-C34-C33	118.2(7)
C18-C17-C6	123.5(6)	C36-C35-C34	122.8(7)
C22-C17-C6	120.6(6)	C37-C36-C35	119.5(7)
O2-C18-C17	116.0(6)	C36-C37-C32	118.8(7)
O2-C18-C19	118.7(6)	C36-C37-C48	122.4(6)
C17-C18-C19	125.3(6)	C32-C37-C48	118.7(6)
C20-C19-C18	114.3(6)	C43-C38-C39	116.5(7)
C20-C19-C23	120.7(6)	C43-C38-C33	119.6(7)
C18-C19-C23	125.1(6)	C39-C38-C33	123.9(6)
C21-C20-C19	122.8(7)	O3-C39-C38	118.2(6)
C22-C21-C20	121.0(7)	O3-C39-C40	119.3(6)
C21-C22-C17	120.5(7)	C38-C39-C40	122.5(6)
C25-C23-C24	108.6(7)	C41-C40-C39	116.1(7)
C25-C23-C26	106.0(6)	C41-C40-C44	122.1(7)
C24-C23-C26	107.2(6)	C39-C40-C44	121.8(6)
C25-C23-C19	111.8(6)	C40-C41-C42	123.0(7)
C24-C23-C19	111.2(6)	C43-C42-C41	119.5(7)
C26-C23-C19	111.8(6)	C42-C43-C38	122.3(7)
C28-C27-W1	143.5(5)	C45-C44-C46	109.4(7)
C31-C28-C27	111.6(6)	C45-C44-C47	107.7(7)
C31-C28-C30	111.4(7)	C46-C44-C47	107.1(7)
C27-C28-C30	108.2(6)	C45-C44-C40	110.2(6)
C31-C28-C29	109.7(7)	C46-C44-C40	110.8(6)
C27-C28-C29	107.6(6)	C47-C44-C40	111.5(6)

Table B-16: Continued

Bond	Angle	Bond	Angle
C30-C28-C29	108.3(6)	C53-C48-C49	117.4(7)
C53-C48-C37	120.6(7)	C65-C64-C69	116.4(7)
C49-C48-C37	122.0(6)	C65-C64-C59	121.3(7)
O4-C49-C50	119.7(6)	C69-C64-C59	122.3(7)
O4-C49-C48	117.7(6)	O5-C65-C66	120.7(6)
C50-C49-C48	122.6(6)	O5-C65-C64	116.3(6)
C51-C50-C49	116.0(7)	C66-C65-C64	123.0(7)
C51-C50-C54	120.8(7)	C65-C66-C67	115.9(7)
C49-C50-C54	123.2(6)	C65-C66-C70	124.0(7)
C52-C51-C50	123.4(7)	C67-C66-C70	120.1(7)
C51-C52-C53	119.4(7)	C68-C67-C66	122.7(8)
C48-C53-C52	121.1(8)	C69-C68-C67	120.0(8)
C55-C54-C57	105.7(8)	C68-C69-C64	121.4(7)
C55-C54-C50	110.6(7)	C72-C70-C73	108.0(9)
C57-C54-C50	113.0(7)	C72-C70-C71	107.1(11)
C55-C54-C56	110.7(8)	C73-C70-C71	105.1(8)
C57-C54-C56	108.0(7)	C72-C70-C66	110.4(7)
C50-C54-C56	108.7(7)	C73-C70-C66	113.7(7)
C63-C58-C59	117.0(7)	C71-C70-C66	112.1(7)
C63-C58-W2	125.3(6)	C79-C74-C75	115.9(7)
C59-C58-W2	117.5(5)	C79-C74-C63	121.3(7)
C60-C59-C58	120.8(7)	C75-C74-C63	122.8(7)
C60-C59-C64	115.5(7)	O6-C75-C76	119.6(7)
C58-C59-C64	123.7(6)	O6-C75-C74	115.4(7)
C61-C60-C59	121.2(8)	C76-C75-C74	124.9(7)
C62-C61-C60	119.3(8)	C77-C76-C75	116.0(8)
C61-C62-C63	122.4(8)	C77-C76-C80	120.6(8)

Table B-16: Continued

Bond	Angle	Bond	Angle
C58-C63-C62	119.1(8)		
C58-C63-C74	124.4(7)		
C62-C63-C74	116.5(7)		
C78-C79-C74	120.1(8)		
C82-C80-C83	110.4(7)		
C82-C80-C76	110.4(6)		
C83-C80-C76	109.9(6)		
C82-C80-C81	107.8(7)		
C83-C80-C81	106.8(7)		
C76-C80-C81	111.5(7)		
C85-C84-W2	145.7(6)		
C87-C85-C84	109.1(6)		
C87-C85-C88	110.6(7)		
C84-C85-C88	108.9(6)		
C87-C85-C86	109.1(7)		
C84-C85-C86	109.5(6)		
C88-C85-C86	109.6(6)		
C75-C76-C80	123.4(7)		
C76-C77-C78	121.0(8)		
C79-C78-C77	122.1(8)		

Table B-17: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for {[^{t}BuOCO](CH$_3$)$_3$CCH=}W(μ-^{t}BuOCHO)W{=CHC(CH$_3$)$_3$[^{t}BuOCO]} (**5**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

Atom	**U^{11}**	**U^{22}**	**U^{33}**	**U^{23}**	**U^{13}**	**U^{12}**
W1	23(1)	23(1)	23(1)	2(1)	4(1)	-2(1)
W2	34(1)	18(1)	23(1)	0(1)	7(1)	1(1)
O1	24(3)	22(3)	37(3)	5(2)	7(2)	-1(2)
O2	31(3)	22(3)	18(3)	2(2)	2(2)	-1(2)
O3	26(3)	30(3)	22(3)	-1(2)	5(2)	-6(2)
O4	37(3)	21(3)	30(3)	1(2)	9(2)	-4(2)
O5	35(3)	21(3)	23(3)	5(2)	11(2)	-1(2)
O6	40(3)	19(3)	32(3)	-2(2)	5(2)	1(2)
C1	27(4)	19(4)	25(4)	-7(3)	10(3)	-2(3)
C2	24(4)	24(4)	24(4)	-6(3)	6(3)	-1(3)
C3	27(5)	26(4)	33(5)	-2(4)	8(4)	0(3)
C4	23(4)	40(5)	27(5)	3(4)	-4(3)	-5(4)
C5	36(5)	40(5)	22(4)	0(4)	3(4)	7(4)
C6	31(5)	23(4)	24(4)	-8(3)	7(4)	6(4)
C7	30(5)	20(4)	29(5)	-2(3)	11(4)	-7(3)
C8	36(5)	17(4)	33(5)	-1(3)	12(4)	-10(3)
C9	33(5)	31(5)	28(5)	1(4)	0(4)	-7(4)
C10	43(5)	26(5)	36(5)	1(4)	1(4)	-7(4)
C11	33(5)	47(5)	44(6)	12(4)	12(4)	-10(4)
C12	36(5)	32(5)	34(5)	2(4)	6(4)	-3(4)
C13	33(5)	39(5)	37(5)	6(4)	0(4)	-3(4)
C14	67(8)	93(9)	91(9)	-20(7)	-41(6)	26(7)
C15	69(7)	37(6)	103(8)	39(5)	27(6)	14(5)
C16	58(7)	62(6)	69(7)	32(5)	26(5)	33(5)
C17	25(4)	19(4)	26(4)	-1(3)	4(3)	8(3)
C18	25(4)	24(4)	19(4)	1(3)	7(3)	5(3)

Table B-17: Continued

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C19	26(4)	21(4)	26(4)	1(4)	4(3)	3(4)
C20	34(5)	25(4)	41(5)	12(4)	12(4)	-10(4)
C21	48(5)	31(5)	23(5)	12(3)	2(4)	-3(4)
C22	28(4)	36(5)	17(4)	3(3)	-3(3)	0(4)
C23	34(5)	25(4)	27(5)	-2(3)	2(4)	-7(4)
C24	87(8)	82(7)	42(6)	-31(5)	23(6)	-40(6)
C25	45(6)	47(6)	60(7)	-1(5)	-9(5)	-15(5)
C26	52(6)	36(5)	53(6)	6(4)	0(5)	-13(4)
C27	31(4)	21(4)	31(5)	5(3)	-1(3)	-7(3)
C28	40(5)	31(5)	25(5)	3(4)	8(4)	-2(4)
C29	42(6)	53(6)	60(6)	-5(5)	22(5)	-1(5)
C30	68(7)	47(6)	45(6)	-14(4)	13(5)	-5(5)
C31	66(7)	39(5)	51(6)	2(4)	22(5)	17(5)
C32	25(4)	26(4)	29(5)	-3(3)	0(4)	11(3)
C33	29(4)	27(4)	21(4)	-4(3)	10(3)	1(3)
C34	38(5)	24(4)	20(4)	3(3)	7(4)	10(4)
C35	37(5)	42(5)	24(5)	3(4)	0(4)	13(4)
C36	33(5)	26(4)	29(5)	-11(4)	0(4)	2(4)
C37	26(4)	25(4)	18(4)	-9(3)	1(3)	4(3)
C38	26(4)	14(4)	37(5)	4(3)	6(4)	3(3)
C39	32(4)	13(4)	24(4)	1(3)	8(3)	1(3)
C40	22(4)	28(4)	36(5)	2(4)	4(3)	2(4)
C41	32(5)	45(5)	43(6)	13(4)	5(4)	2(4)
C42	32(5)	34(5)	55(6)	12(4)	22(4)	5(4)
C43	37(5)	29(5)	34(5)	2(4)	12(4)	7(4)
C44	31(5)	53(6)	37(5)	-1(4)	1(4)	0(4)
C45	64(7)	66(7)	33(5)	30(5)	0(5)	4(5)

Table B-17: Continued

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C46	51(6)	68(7)	43(6)	-14(5)	6(5)	-3(5)
C47	36(6)	127(9)	46(6)	16(6)	-9(4)	-1(6)
C48	24(4)	30(4)	18(4)	-9(3)	-1(3)	2(4)
C49	18(4)	37(5)	16(4)	1(3)	-1(3)	3(3)
C50	32(5)	26(5)	31(5)	2(3)	3(4)	-6(4)
C51	36(5)	34(5)	60(6)	6(4)	11(4)	-6(4)
C52	26(5)	67(7)	62(6)	5(5)	18(4)	-12(5)
C53	30(5)	46(5)	41(5)	-10(4)	1(4)	4(4)
C54	50(6)	14(4)	74(7)	7(4)	16(5)	-7(4)
C55	179(13)	32(6)	103(10)	-29(6)	56(9)	-15(7)
C56	53(7)	33(6)	194(13)	23(7)	12(8)	19(5)
C57	91(9)	23(5)	123(10)	15(5)	19(7)	-12(5)
C58	44(5)	20(4)	17(4)	1(3)	10(4)	14(4)
C59	49(5)	29(4)	17(4)	-3(3)	13(4)	-6(4)
C60	58(6)	34(5)	28(5)	2(4)	12(4)	-18(4)
C61	73(7)	30(5)	53(6)	5(4)	11(5)	-13(5)
C62	63(7)	44(6)	42(6)	17(4)	4(5)	-2(5)
C63	54(6)	26(4)	27(5)	8(4)	21(4)	3(4)
C64	37(5)	30(5)	18(4)	-3(3)	3(3)	-8(4)
C65	33(5)	20(4)	16(4)	-4(3)	5(3)	1(3)
C66	24(4)	32(5)	28(5)	-7(3)	-6(4)	0(4)
C67	40(6)	61(6)	31(5)	-2(4)	-9(4)	5(5)
C68	30(5)	67(6)	40(6)	-1(5)	1(4)	-4(5)
C69	53(6)	55(6)	35(5)	-4(5)	16(5)	-24(5)
C70	47(5)	37(5)	25(5)	9(4)	3(4)	10(4)
C71	244(18)	223(16)	119(11)	131(11)	144(12)	199(15)
C72	350(20)	128(12)	53(8)	47(8)	-57(10)	-179(14)

Table B-17: Continued

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C73	67(8)	149(11)	54(7)	45(7)	5(6)	12(8)
C74	40(5)	27(4)	22(4)	-3(3)	12(4)	12(4)
C75	48(5)	21(4)	24(4)	-3(3)	11(4)	12(4)
C76	42(5)	39(5)	30(5)	-3(4)	2(4)	11(4)
C77	50(6)	51(6)	30(5)	-8(4)	2(4)	10(5)
C78	56(7)	76(7)	25(5)	3(5)	2(5)	36(6)
C79	65(7)	30(5)	42(6)	4(4)	11(5)	12(5)
C80	37(5)	42(5)	33(5)	-5(4)	-1(4)	-6(4)
C81	57(7)	73(7)	49(6)	-11(5)	-14(5)	-12(5)
C82	56(6)	40(5)	48(6)	-5(4)	10(5)	-7(4)
C83	58(6)	43(6)	67(7)	-31(5)	16(5)	-2(5)
C84	37(5)	20(4)	27(5)	3(3)	7(4)	4(3)
C85	45(5)	22(4)	28(5)	0(4)	10(4)	6(4)
C86	65(6)	56(6)	28(5)	-9(4)	13(4)	14(5)
C87	80(7)	41(5)	48(6)	-14(4)	20(5)	0(5)
C88	56(6)	59(6)	42(6)	0(5)	22(5)	11(5)

Table B-18: Torsion angles (in deg) for {[^{t}BuOCO](CH$_3$)$_3$CCH=}W(μ-^{t}BuOCHO) W{=CHC(CH$_3$)$_3$[^{t}BuOCO]} (**5**)

Atoms	Angle	Atoms	Angle
O2-W1-O1-C8	110.8(6)	O3-W1-C1-C2	-105.3(6)
C27-W1-O1-C8	-37.7(6)	O2-W1-C1-C6	-18.1(5)
O3-W1-O1-C8	-149.8(5)	C27-W1-C1-C6	-121.9(5)
C1-W1-O1-C8	58.0(5)	O1-W1-C1-C6	145.1(5)
C27-W1-O2-C18	120.3(7)	O3-W1-C1-C6	70.8(7)
O1-W1-O2-C18	-27.1(10)	C6-C1-C2-C3	-1.6(9)
O3-W1-O2-C18	-125.2(7)	W1-C1-C2-C3	174.6(5)
C1-W1-O2-C18	25.7(7)	C6-C1-C2-C7	-179.0(6)
O2-W1-O3-C39	41.0(6)	W1-C1-C2-C7	-2.7(8)
C27-W1-O3-C39	148.8(6)	C1-C2-C3-C4	0.7(10)
O1-W1-O3-C39	-118.1(6)	C7-C2-C3-C4	178.2(6)
C1-W1-O3-C39	-44.8(8)	C2-C3-C4-C5	1.3(11)
O6-W2-O4-C49	54.1(8)	C3-C4-C5-C6	-2.2(11)
C84-W2-O4-C49	160.2(8)	C4-C5-C6-C1	1.2(10)
O5-W2-O4-C49	-103.6(8)	C4-C5-C6-C17	178.2(6)
C58-W2-O4-C49	-30.2(12)	C2-C1-C6-C5	0.8(9)
O6-W2-O5-C65	115.8(6)	W1-C1-C6-C5	-175.3(5)
C84-W2-O5-C65	-35.2(5)	C2-C1-C6-C17	-176.0(6)
O4-W2-O5-C65	-142.3(5)	W1-C1-C6-C17	7.9(9)
C58-W2-O5-C65	59.7(5)	C3-C2-C7-C12	31.8(9)
C84-W2-O6-C75	110.4(8)	C1-C2-C7-C12	-150.8(7)
O5-W2-O6-C75	-39.8(11)	C3-C2-C7-C8	-144.3(7)
O4-W2-O6-C75	-140.4(8)	C1-C2-C7-C8	33.1(10)
C58-W2-O6-C75	16.7(8)	W1-O1-C8-C7	-44.8(8)
O2-W1-C1-C2	165.8(5)	W1-O1-C8-C9	136.5(5)
C27-W1-C1-C2	62.0(5)	C12-C7-C8-O1	172.4(6)
O1-W1-C1-C2	-31.0(5)	C2-C7-C8-O1	-11.3(10)

Table B-18: Continued

Atoms	Angle	Atoms	Angle
C12-C7-C8-C9	-9.0(10)	C17-C18-C19-C20	4.1(10)
C2-C7-C8-C9	167.3(6)	O2-C18-C19-C23	6.8(10)
O1-C8-C9-C10	-173.1(6)	C17-C18-C19-C23	-175.8(6)
C7-C8-C9-C10	8.3(10)	C18-C19-C20-C21	0.4(10)
O1-C8-C9-C13	3.3(10)	C23-C19-C20-C21	-179.7(7)
C7-C8-C9-C13	-175.3(7)	C19-C20-C21-C22	-2.8(12)
C8-C9-C10-C11	-1.8(11)	C20-C21-C22-C17	1.0(11)
C13-C9-C10-C11	-178.3(7)	C18-C17-C22-C21	3.1(10)
C9-C10-C11-C12	-3.7(12)	C6-C17-C22-C21	-175.0(6)
C10-C11-C12-C7	3.2(12)	C20-C19-C23-C25	116.2(7)
C8-C7-C12-C11	2.9(11)	C18-C19-C23-C25	-63.9(9)
C2-C7-C12-C11	-173.3(7)	C20-C19-C23-C24	-122.2(8)
C10-C9-C13-C14	90.4(9)	C18-C19-C23-C24	57.7(9)
C8-C9-C13-C14	-85.7(9)	C20-C19-C23-C26	-2.5(9)
C10-C9-C13-C16	-146.1(7)	C18-C19-C23-C26	177.4(6)
C8-C9-C13-C16	37.8(11)	O2-W1-C27-C28	-22.5(9)
C10-C9-C13-C15	-28.3(10)	O1-W1-C27-C28	146.3(9)
C8-C9-C13-C15	155.6(7)	O3-W1-C27-C28	-124.3(8)
C5-C6-C17-C18	-166.0(6)	C1-W1-C27-C28	62.2(9)
C1-C6-C17-C18	10.8(10)	W1-C27-C28-C31	7.3(12)
C5-C6-C17-C22	11.9(9)	W1-C27-C28-C30	130.2(8)
C1-C6-C17-C22	-171.4(6)	W1-C27-C28-C29	-113.0(8)
W1-O2-C18-C17	-14.9(10)	C37-C32-C33-C34	1.8(10)
W1-O2-C18-C19	162.7(5)	C37-C32-C33-C38	172.6(6)
C22-C17-C18-O2	171.7(5)	C32-C33-C34-C35	-2.0(10)
C6-C17-C18-O2	-10.4(9)	C38-C33-C34-C35	-172.9(6)
C22-C17-C18-C19	-5.8(10)	C33-C34-C35-C36	1.1(10)

Table B-18: Continued

Atoms	Angle	Atoms	Angle
C6-C17-C18-C19	172.2(6)	C34-C35-C36-C37	0.1(11)
O2-C18-C19-C20	-173.3(6)	C35-C36-C37-C32	-0.4(10)
C35-C36-C37-C48	-177.7(6)	C36-C37-C48-C53	77.8(9)
C33-C32-C37-C36	-0.6(10)	C32-C37-C48-C53	-99.6(8)
C33-C32-C37-C48	176.9(6)	C36-C37-C48-C49	-103.6(8)
C32-C33-C38-C43	-116.4(7)	C32-C37-C48-C49	79.0(8)
C34-C33-C38-C43	54.4(9)	W2-O4-C49-C50	-156.0(6)
C32-C33-C38-C39	61.9(9)	W2-O4-C49-C48	23.8(11)
C34-C33-C38-C39	-127.4(7)	C53-C48-C49-O4	-176.8(6)
W1-O3-C39-C38	33.5(9)	C37-C48-C49-O4	4.6(9)
W1-O3-C39-C40	-143.2(6)	C53-C48-C49-C50	3.0(10)
C43-C38-C39-O3	-173.5(6)	C37-C48-C49-C50	-175.6(7)
C33-C38-C39-O3	8.2(9)	O4-C49-C50-C51	178.1(7)
C43-C38-C39-C40	3.2(9)	C48-C49-C50-C51	-1.6(11)
C33-C38-C39-C40	-175.2(6)	O4-C49-C50-C54	0.3(11)
O3-C39-C40-C41	174.2(6)	C48-C49-C50-C54	-179.5(7)
C38-C39-C40-C41	-2.4(10)	C49-C50-C51-C52	0.3(12)
O3-C39-C40-C44	-8.6(10)	C54-C50-C51-C52	178.2(8)
C38-C39-C40-C44	174.8(6)	C50-C51-C52-C53	-0.5(13)
C39-C40-C41-C42	-0.7(11)	C49-C48-C53-C52	-3.1(11)
C44-C40-C41-C42	-177.9(7)	C37-C48-C53-C52	175.5(7)
C40-C41-C42-C43	2.8(12)	C51-C52-C53-C48	1.9(12)
C41-C42-C43-C38	-2.0(12)	C51-C50-C54-C55	-116.1(9)
C39-C38-C43-C42	-0.9(10)	C49-C50-C54-C55	61.7(10)
C33-C38-C43-C42	177.5(7)	C51-C50-C54-C57	2.3(11)
C41-C40-C44-C45	119.1(8)	C49-C50-C54-C57	-180.0(8)
C39-C40-C44-C45	-58.0(9)	C51-C50-C54-C56	122.2(9)

Table B-18: Continued

Atoms	Angle	Atoms	Angle
C41-C40-C44-C46	-119.7(8)	C49-C50-C54-C56	-60.0(10)
C39-C40-C44-C46	63.3(9)	O6-W2-C58-C63	-14.6(6)
C41-C40-C44-C47	-0.5(11)	C84-W2-C58-C63	-117.6(6)
C39-C40-C44-C47	-177.5(7)	O5-W2-C58-C63	146.6(6)
O4-W2-C58-C63	72.4(9)	O5-C65-C66-C67	-171.3(6)
O6-W2-C58-C59	171.3(5)	C64-C65-C66-C67	8.2(10)
C84-W2-C58-C59	68.2(5)	O5-C65-C66-C70	8.5(10)
O5-W2-C58-C59	-27.6(5)	C64-C65-C66-C70	-172.0(7)
O4-W2-C58-C59	-101.8(7)	C65-C66-C67-C68	-2.3(11)
C63-C58-C59-C60	-4.6(10)	C70-C66-C67-C68	177.9(7)
W2-C58-C59-C60	170.1(5)	C66-C67-C68-C69	-3.5(13)
C63-C58-C59-C64	176.5(6)	C67-C68-C69-C64	3.7(13)
W2-C58-C59-C64	-8.8(9)	C65-C64-C69-C68	1.8(11)
C58-C59-C60-C61	1.4(11)	C59-C64-C69-C68	-176.6(7)
C64-C59-C60-C61	-179.6(7)	C65-C66-C70-C72	-72.9(11)
C59-C60-C61-C62	2.0(12)	C67-C66-C70-C72	106.8(11)
C60-C61-C62-C63	-2.1(13)	C65-C66-C70-C73	165.5(8)
C59-C58-C63-C62	4.4(10)	C67-C66-C70-C73	-14.7(11)
W2-C58-C63-C62	-169.8(5)	C65-C66-C70-C71	46.4(12)
C59-C58-C63-C74	-173.9(6)	C67-C66-C70-C71	-133.8(10)
W2-C58-C63-C74	11.9(10)	C58-C63-C74-C79	178.7(7)
C61-C62-C63-C58	-1.2(12)	C62-C63-C74-C79	0.3(10)
C61-C62-C63-C74	177.2(8)	C58-C63-C74-C75	-0.3(10)
C60-C59-C64-C65	-141.7(7)	C62-C63-C74-C75	-178.7(6)
C58-C59-C64-C65	37.2(10)	W2-O6-C75-C76	169.2(6)
C60-C59-C64-C69	36.6(10)	W2-O6-C75-C74	-10.2(11)
C58-C59-C64-C69	-144.4(7)	C79-C74-C75-O6	177.9(6)

Table B-18: Continued

Atoms	Angle	Atoms	Angle
W2-O5-C65-C66	131.2(5)	C63-C74-C75-O6	-3.1(9)
W2-O5-C65-C64	-48.4(7)	C79-C74-C75-C76	-1.4(10)
C69-C64-C65-O5	171.5(6)	C63-C74-C75-C76	177.6(7)
C59-C64-C65-O5	-10.0(9)	O6-C75-C76-C77	-179.1(6)
C69-C64-C65-C66	-8.0(10)	C74-C75-C76-C77	0.2(11)
C59-C64-C65-C66	170.4(6)	O6-C75-C76-C80	1.6(11)
C74-C75-C76-C80	-179.1(6)		
C75-C76-C77-C78	1.1(11)		
C80-C76-C77-C78	-179.5(7)		
C76-C77-C78-C79	-1.3(12)		
C77-C78-C79-C74	0.0(12)		
C75-C74-C79-C78	1.2(11)		
C63-C74-C79-C78	-177.8(7)		
C77-C76-C80-C82	116.0(8)		
C75-C76-C80-C82	-64.7(9)		
C77-C76-C80-C83	-121.9(8)		
C75-C76-C80-C83	57.4(10)		
C77-C76-C80-C81	-3.7(10)		
C75-C76-C80-C81	175.6(7)		
O6-W2-C84-C85	-20.8(9)		
O5-W2-C84-C85	148.1(9)		
O4-W2-C84-C85	-121.1(9)		
C58-W2-C84-C85	62.9(9)		
W2-C84-C85-C87	115.2(9)		
W2-C84-C85-C88	-124.0(9)		
W2-C84-C85-C86	-4.2(12)		
C63-C74-C75-O6	-3.1(9)		

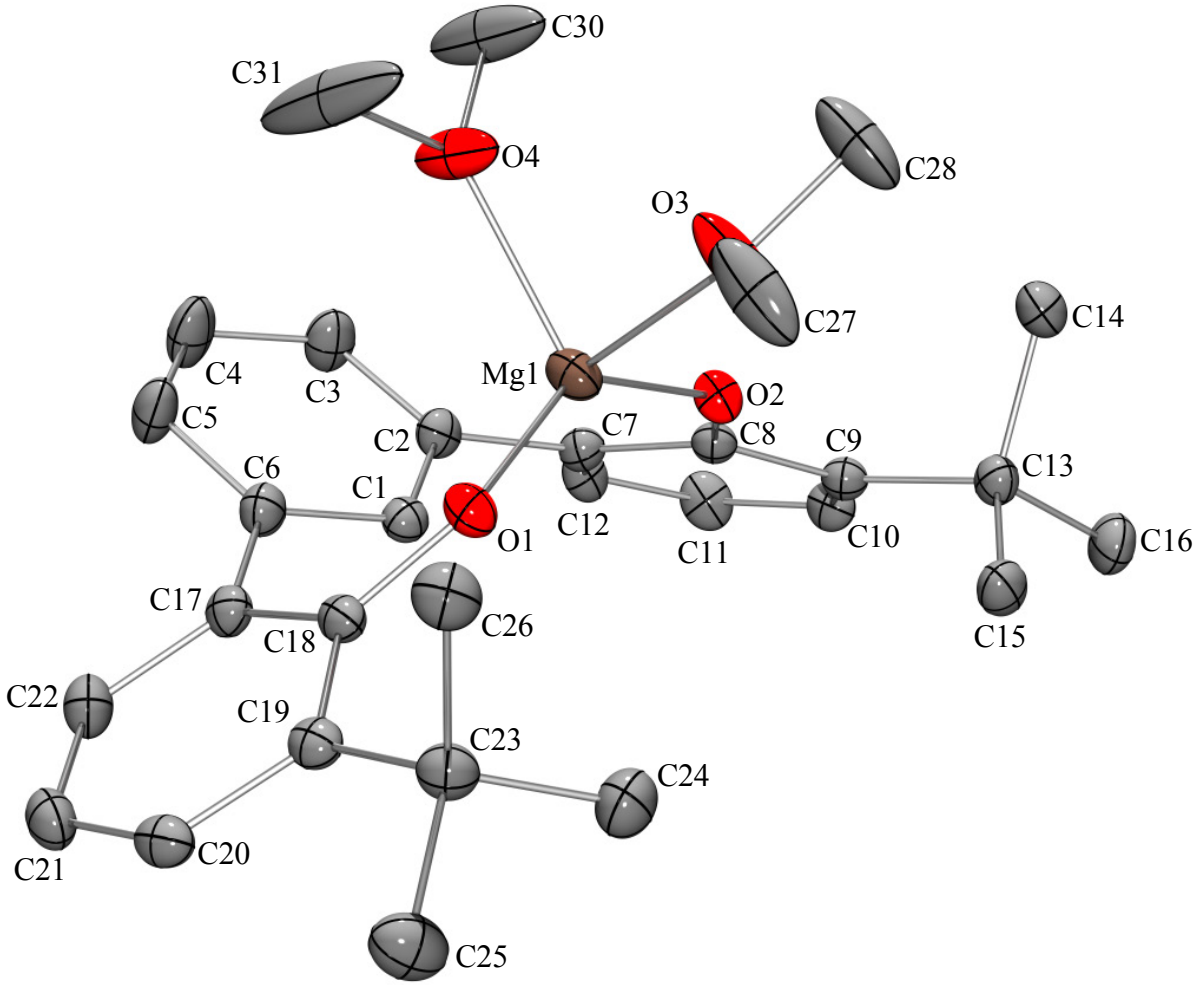


Figure B-5: Asymetric unit of $[(^{t}BuOCHO)Mg\{O(CH_2CH_2)_2O\}]_n$ (**6**). Ellipsoids are shown at 30% probability level. Benzene and hydrogens omitted for clarity.

X-ray Experimental for $[(^{t}BuOCHO)Mg\{O(CH_2CH_2)_2O\}]_n$ (6)

Data were collected at 173 K on a Siemens SMART PLATFORM equipped with A CCD area detector and a graphite monochromator utilizing MoKα radiation (λ = 0.71073 Å). Cell parameters were refined using up to 8192 reflections. A full sphere of data (1850 frames) was collected using the ω-scan method (0.3°frame width). The first 50 frames were re-measured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was < 1 %). Absorption corrections by integration were applied based on measured indexed crystal faces.

The structure was solved by the author using Direct Methods in *SHELXTL6,* and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. A total of 865 parameters were refined in the final cycle of refinement using 8981 reflections (with $I > 2\sigma I$) to yield R_1 and wR_2 of 4.85% and 9.19%, respectively. Refinement was done using F^2.

Table B-19: Crystal data, structure solution, and refinement for [(^{t}BuOCHO)Mg-{O(CH_2CH_2)$_2$O}]$_n$ (**6**)

identification code	pelo11
empirical formula	$C_{35}H_{43}O_5Mg$
formula weight	568.00
T (K)	173(2)
λ (Å)	0.71073
crystal system	Triclinic
Space group	P-1
a (Å)	9.9603(13)
b (Å)	13.3947(16)
c (Å)	13.4559(13)
α (deg)	69.908(2)
β (deg)	70.504(2)
γ (deg)	72.835(2)
V (Å^3)	1555.9(3)
Z	2
ρ_{calcd}(g mm^{-3})	1.212
crystal size (mm)	0.34 x 0.09 x 0.05
abs coeff (mm^{-1})	0.097
F(000)	610
θ range for data collection (deg)	1.67 to 27.50
limiting indices	$-12 \le h \le 12$, $-14 \le k \le 17$, $-17 \le l \le 15$
no. of reflns collcd	10652
no. of ind reflns (R_{int})	6970 (0.0470)
completeness to θ= 27.50°	97.7 %
absorption corr	Integration
refinement method	Full-matrix least-squares on F^2
data / restraints / parameters	6970 / 0 / 370
$R1$, $wR2$ [$I > 2\sigma$]	0.0578, 0.1432
$R1$, $wR2$ (all data)	0.1128, 0.1642
GOF on F^2	0.933
largest diff. peak and hole (e.Å^{-3})	0.628 and -0.620

$R1 = \Sigma(||F_o| - |F_c||) / \Sigma|F_o|$

$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

$S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$

$w = 1/[\sigma^2(F_o^2)+(m*p)^2+n*p]$, $p = [\max(F_o^2,0)+ 2* F_c^2]/3$, m & n are constants.

Table B-20: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for [(^{t}BuOCHO)Mg{O(CH_2CH_2)$_2$O}]$_n$ (**6**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	X	Y	Z	U(eq)
Mg1	8144(1)	5557(1)	3134(1)	33(1)
O1	9182(2)	4320(1)	2634(1)	32(1)
O2	8222(2)	7031(1)	2822(1)	30(1)
O3	8968(3)	5057(2)	4474(2)	73(1)
O4	6137(2)	5303(1)	4111(2)	62(1)
C1	7349(3)	6171(2)	1434(2)	28(1)
C2	6313(3)	7104(2)	1605(2)	31(1)
C3	4855(3)	7085(2)	1785(2)	43(1)
C4	4479(3)	6164(2)	1780(3)	51(1)
C5	5512(3)	5244(2)	1650(2)	44(1)
C6	6978(3)	5226(2)	1470(2)	32(1)
C7	6783(2)	8076(2)	1561(2)	28(1)
C8	7816(2)	7974(2)	2118(2)	25(1)
C9	8382(2)	8903(2)	1940(2)	28(1)
C10	7806(3)	9888(2)	1284(2)	34(1)
C11	6721(3)	9995(2)	804(2)	39(1)
C12	6229(3)	9089(2)	936(2)	34(1)
C13	9551(3)	8832(2)	2485(2)	32(1)
C14	8865(3)	8666(2)	3723(2)	38(1)
C15	10855(3)	7909(2)	2270(2)	38(1)
C16	10160(3)	9876(2)	2051(2)	47(1)
C17	8143(3)	4263(2)	1294(2)	29(1)
C18	9269(3)	3895(2)	1842(2)	28(1)
C19	10454(3)	3054(2)	1553(2)	30(1)
C20	10385(3)	2568(2)	811(2)	34(1)
C21	9244(3)	2881(2)	334(2)	37(1)

Table B-20: Continued

Atom	X	Y	Z	U(eq)
C22	8140(3)	3733(2)	566(2)	36(1)
C23	11753(3)	2658(2)	2065(2)	34(1)
C24	12389(3)	3620(2)	1955(2)	44(1)
C25	13006(3)	1878(2)	1514(2)	48(1)
C26	11246(3)	2026(2)	3274(2)	40(1)
C27	10015(5)	4060(2)	4786(3)	73(1)
C28	8620(5)	5695(2)	5234(3)	74(1)
C29	5789(5)	4249(3)	4473(4)	156(3)
C30	4957(4)	6083(2)	4570(3)	107(2)
C31	7419(3)	1690(2)	3952(3)	55(1)
C32	7643(3)	1291(2)	4981(3)	57(1)
C33	6531(3)	958(2)	5875(3)	55(1)
C34	5205(3)	1029(2)	5733(3)	56(1)
C35	4986(3)	1415(3)	4706(3)	61(1)
C36	6099(4)	1756(2)	3804(3)	59(1)

Table B-21: Bond lengths (in Å) for [(^{t}BuOCHO)Mg{O(CH_2CH_2)$_2$O}]$_n$ (**6**)

Bond	Length	Bond	Length
Mg1-O1	1.8857(17)	C11-C12	1.375(3)
Mg1-O2	1.8915(17)	C13-C15	1.532(3)
Mg1-O4	2.044(2)	C13-C14	1.539(3)
Mg1-O3	2.050(2)	C13-C16	1.539(3)
Mg1-C1	2.464(2)	C17-C22	1.394(3)
O1-C18	1.340(3)	C17-C18	1.422(3)
O2-C8	1.338(3)	C18-C19	1.422(3)
O3-C28	1.445(3)	C19-C20	1.394(3)
O3-C27	1.461(3)	C19-C23	1.538(3)
O4-C29	1.432(4)	C20-C21	1.379(3)
O4-C30	1.445(3)	C21-C22	1.372(3)
C1-C2	1.399(3)	C23-C25	1.530(3)
C1-C6	1.401(3)	C23-C24	1.541(3)
C2-C3	1.396(3)	C23-C26	1.542(3)
C2-C7	1.485(3)	C27-C28#1	1.480(5)
C3-C4	1.393(3)	C28-C27#1	1.480(5)
C4-C5	1.375(4)	C29-C30#2	1.254(5)
C5-C6	1.392(3)	C30-C29#2	1.254(5)
C6-C17	1.487(3)	C31-C36	1.368(4)
C7-C12	1.391(3)	C31-C32	1.371(4)
C7-C8	1.414(3)	C32-C33	1.381(4)
C8-C9	1.430(3)	C33-C34	1.368(4)
C9-C10	1.393(3)	C34-C35	1.368(4)
C9-C13	1.535(3)	C35-C36	1.390(4)
C10-C11	1.384(3)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+1 #2 -x+1,-y+1,-z+1

Table B-22: Bond angles (in deg) for [(^{t}BuOCHO)Mg{O(CH_2CH_2)$_2$O}]$_n$ (**6**)

Bond	Angle	Bond	Angle
O1-Mg1-O2	139.75(8)	C5-C6-C17	122.7(2)
O1-Mg1-O4	109.39(8)	C1-C6-C17	119.7(2)
O2-Mg1-O4	109.60(8)	C12-C7-C8	120.2(2)
O1-Mg1-O3	94.36(8)	C12-C7-C2	119.2(2)
O2-Mg1-O3	94.47(8)	C8-C7-C2	120.6(2)
O4-Mg1-O3	91.16(11)	O2-C8-C7	120.4(2)
O1-Mg1-C1	83.87(8)	O2-C8-C9	120.7(2)
O2-Mg1-C1	84.30(7)	C7-C8-C9	118.9(2)
O4-Mg1-C1	93.34(9)	C10-C9-C8	117.9(2)
O3-Mg1-C1	175.49(10)	C10-C9-C13	120.8(2)
C18-O1-Mg1	138.27(15)	C8-C9-C13	121.3(2)
C8-O2-Mg1	137.33(15)	C11-C10-C9	122.7(2)
C28-O3-C27	109.7(2)	C12-C11-C10	119.1(2)
C28-O3-Mg1	123.37(19)	C11-C12-C7	121.0(2)
C27-O3-Mg1	126.87(16)	C15-C13-C9	111.49(19)
C29-O4-C30	111.9(2)	C15-C13-C14	110.5(2)
C29-O4-Mg1	121.05(18)	C9-C13-C14	108.75(19)
C30-O4-Mg1	126.99(17)	C15-C13-C16	106.3(2)
C2-C1-C6	122.9(2)	C9-C13-C16	112.4(2)
C2-C1-Mg1	99.79(15)	C14-C13-C16	107.26(19)
C6-C1-Mg1	100.38(15)	C22-C17-C18	120.0(2)
C3-C2-C1	117.5(2)	C22-C17-C6	119.4(2)
C3-C2-C7	122.5(2)	C18-C17-C6	120.6(2)
C1-C2-C7	120.0(2)	O1-C18-C17	120.0(2)
C4-C3-C2	120.1(2)	O1-C18-C19	121.2(2)
C5-C4-C3	121.3(2)	C17-C18-C19	118.8(2)
C4-C5-C6	120.5(2)	C20-C19-C18	117.8(2)
C5-C6-C1	117.7(2)	C20-C19-C23	120.4(2)

Table B-22: Continued

Bond	Angle	Bond	Angle
C18-C19-C23	121.8(2)		
C21-C20-C19	123.1(2)		
C22-C21-C20	119.1(2)		
C21-C22-C17	120.9(2)		
C25-C23-C19	113.0(2)		
C25-C23-C24	106.3(2)		
C19-C23-C24	110.7(2)		
C25-C23-C26	106.6(2)		
C19-C23-C26	108.8(2)		
C24-C23-C26	111.4(2)		
O3-C27-C28#1	111.0(3)		
O3-C28-C27#1	108.2(3)		
C30#2-C29-O4	120.1(4)		
C29#2-C30-O4	117.5(3)		
C36-C31-C32	120.3(3)		
C31-C32-C33	120.1(3)		
C34-C33-C32	119.9(3)		
C35-C34-C33	120.1(3)		
C34-C35-C36	120.2(3)		
C31-C36-C35	119.4(3)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+1 #2 -x+1,-y+1,-z+1

Table B-23: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for [(^{t}BuOCHO)Mg-{O(CH_2CH_2)$_2$O}]$_n$ (**6**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

Atom	**U^{11}**	**U^{22}**	**U^{33}**	**U^{23}**	**U^{13}**	**U^{12}**
Mg1	48(1)	24(1)	25(1)	-5(1)	-8(1)	-6(1)
O1	39(1)	28(1)	27(1)	-8(1)	-10(1)	-4(1)
O2	38(1)	22(1)	28(1)	-3(1)	-14(1)	-3(1)
O3	150(2)	28(1)	48(1)	-13(1)	-60(1)	12(1)
O4	73(1)	25(1)	59(1)	-18(1)	30(1)	-17(1)
C1	30(1)	30(1)	23(1)	-4(1)	-8(1)	-7(1)
C2	28(1)	32(1)	32(1)	-8(1)	-11(1)	-3(1)
C3	29(2)	40(2)	63(2)	-21(1)	-14(1)	0(1)
C4	29(2)	50(2)	83(2)	-26(2)	-17(2)	-8(1)
C5	33(2)	39(2)	66(2)	-20(1)	-12(1)	-11(1)
C6	32(1)	33(1)	33(1)	-7(1)	-11(1)	-8(1)
C7	26(1)	25(1)	30(1)	-7(1)	-5(1)	-3(1)
C8	25(1)	24(1)	24(1)	-7(1)	-5(1)	-2(1)
C9	29(1)	26(1)	26(1)	-7(1)	-5(1)	-4(1)
C10	42(2)	23(1)	34(1)	-5(1)	-9(1)	-7(1)
C11	49(2)	23(1)	41(2)	-4(1)	-22(1)	4(1)
C12	35(1)	32(1)	38(2)	-11(1)	-18(1)	3(1)
C13	33(1)	29(1)	35(1)	-10(1)	-8(1)	-8(1)
C14	43(2)	39(2)	36(2)	-13(1)	-13(1)	-6(1)
C15	30(1)	44(2)	43(2)	-16(1)	-12(1)	-4(1)
C16	49(2)	47(2)	51(2)	-13(1)	-13(1)	-21(1)
C17	31(1)	25(1)	31(1)	-6(1)	-7(1)	-9(1)
C18	34(1)	24(1)	24(1)	-6(1)	-3(1)	-11(1)
C19	35(1)	24(1)	25(1)	-2(1)	-4(1)	-9(1)
C20	39(2)	25(1)	30(1)	-7(1)	-1(1)	-6(1)
C21	48(2)	32(1)	35(2)	-11(1)	-11(1)	-12(1)

Table B-23: Continued

Atom	**U^{11}**	**U^{22}**	**U^{33}**	**U^{23}**	**U^{13}**	**U^{12}**
C22	41(2)	33(1)	39(2)	-7(1)	-17(1)	-10(1)
C23	33(1)	31(1)	33(1)	-8(1)	-7(1)	-2(1)
C24	40(2)	46(2)	48(2)	-10(1)	-13(1)	-12(1)
C25	41(2)	51(2)	44(2)	-16(1)	-12(1)	6(1)
C26	43(2)	34(2)	36(2)	-4(1)	-14(1)	-3(1)
C27	146(4)	22(2)	61(2)	-13(1)	-60(2)	11(2)
C28	139(4)	41(2)	49(2)	-19(2)	-47(2)	3(2)
C29	155(4)	34(2)	181(5)	-48(3)	123(4)	-47(2)
C30	114(3)	30(2)	112(3)	-30(2)	71(3)	-23(2)
C31	51(2)	35(2)	70(2)	-19(2)	1(2)	-10(1)
C32	46(2)	46(2)	79(2)	-16(2)	-18(2)	-9(2)
C33	57(2)	41(2)	64(2)	-16(2)	-16(2)	-3(2)
C34	52(2)	47(2)	67(2)	-27(2)	6(2)	-15(2)
C35	44(2)	64(2)	81(3)	-39(2)	-12(2)	-6(2)
C36	66(2)	49(2)	65(2)	-25(2)	-18(2)	-3(2)

Table B-24: Torsion angles (in deg) for [(^{t}BuOCHO)Mg{O(CH_2CH_2)$_2$O}]$_n$ (**6**)

Atoms	Angle	Atoms	Angle
O2-Mg1-O1-C18	-83.1(2)	C6-C1-C2-C3	-2.0(4)
O4-Mg1-O1-C18	81.9(2)	Mg1-C1-C2-C3	-111.2(2)
O3-Mg1-O1-C18	174.7(2)	C6-C1-C2-C7	179.6(2)
C1-Mg1-O1-C18	-9.5(2)	Mg1-C1-C2-C7	70.4(2)
O1-Mg1-O2-C8	82.9(2)	C1-C2-C3-C4	-0.7(4)
O4-Mg1-O2-C8	-82.2(2)	C7-C2-C3-C4	177.7(3)
O3-Mg1-O2-C8	-175.0(2)	C2-C3-C4-C5	3.1(5)
C1-Mg1-O2-C8	9.4(2)	C3-C4-C5-C6	-2.9(5)
O1-Mg1-O3-C28	177.9(3)	C4-C5-C6-C1	0.3(4)
O2-Mg1-O3-C28	37.2(3)	C4-C5-C6-C17	-178.3(3)
O4-Mg1-O3-C28	-72.5(3)	C2-C1-C6-C5	2.2(4)
O1-Mg1-O3-C27	0.9(3)	Mg1-C1-C6-C5	111.1(2)
O2-Mg1-O3-C27	-139.8(3)	C2-C1-C6-C17	-179.2(2)
O4-Mg1-O3-C27	110.4(3)	Mg1-C1-C6-C17	-70.3(2)
O1-Mg1-O4-C29	10.4(4)	C3-C2-C7-C12	-46.9(3)
O2-Mg1-O4-C29	-179.8(3)	C1-C2-C7-C12	131.4(2)
O3-Mg1-O4-C29	-84.6(3)	C3-C2-C7-C8	135.1(3)
C1-Mg1-O4-C29	95.1(3)	C1-C2-C7-C8	-46.6(3)
O1-Mg1-O4-C30	-173.4(3)	Mg1-O2-C8-C7	17.9(3)
O2-Mg1-O4-C30	-3.6(3)	Mg1-O2-C8-C9	-164.09(16)
O3-Mg1-O4-C30	91.5(3)	C12-C7-C8-O2	171.9(2)
C1-Mg1-O4-C30	-88.8(3)	C2-C7-C8-O2	-10.1(3)
O1-Mg1-C1-C2	172.43(16)	C12-C7-C8-C9	-6.1(3)
O2-Mg1-C1-C2	-46.12(15)	C2-C7-C8-C9	171.9(2)
O4-Mg1-C1-C2	63.27(16)	O2-C8-C9-C10	-173.5(2)
O1-Mg1-C1-C6	46.14(16)	C7-C8-C9-C10	4.5(3)
O2-Mg1-C1-C6	-172.41(16)	O2-C8-C9-C13	4.5(3)
O4-Mg1-C1-C6	-63.02(16)	C7-C8-C9-C13	-177.5(2)

Table B-24: Continued

Atoms	Angle	Atoms	Angle
C8-C9-C10-C11	0.0(4)	C18-C19-C20-C21	1.4(3)
C13-C9-C10-C11	-178.0(2)	C23-C19-C20-C21	179.4(2)
C9-C10-C11-C12	-3.0(4)	C19-C20-C21-C22	2.2(4)
C10-C11-C12-C7	1.4(4)	C20-C21-C22-C17	-1.6(4)
C8-C7-C12-C11	3.2(4)	C18-C17-C22-C21	-2.5(4)
C2-C7-C12-C11	-174.8(2)	C6-C17-C22-C21	176.1(2)
C10-C9-C13-C15	-129.7(2)	C20-C19-C23-C25	11.0(3)
C8-C9-C13-C15	52.4(3)	C18-C19-C23-C25	-171.1(2)
C10-C9-C13-C14	108.2(2)	C20-C19-C23-C24	130.1(2)
C8-C9-C13-C14	-69.8(3)	C18-C19-C23-C24	-52.1(3)
C10-C9-C13-C16	-10.4(3)	C20-C19-C23-C26	-107.2(2)
C8-C9-C13-C16	171.6(2)	C18-C19-C23-C26	70.7(3)
C5-C6-C17-C22	46.5(4)	C28-O3-C27-C28#1	-60.5(4)
C1-C6-C17-C22	-132.0(2)	Mg1-O3-C27-C28#1	116.9(3)
C5-C6-C17-C18	-134.8(3)	C27-O3-C28-C27#1	58.8(4)
C1-C6-C17-C18	46.6(3)	Mg1-O3-C28-C27#1	-118.7(3)
Mg1-O1-C18-C17	-17.3(3)	C30-O4-C29-C30#2	-36.1(8)
Mg1-O1-C18-C19	164.52(17)	Mg1-O4-C29-C30#2	140.6(5)
C22-C17-C18-O1	-172.2(2)	C29-O4-C30-C29#2	35.1(8)
C6-C17-C18-O1	9.2(3)	Mg1-O4-C30-C29#2	-141.4(5)
C22-C17-C18-C19	6.1(3)	C36-C31-C32-C33	-0.4(4)
C6-C17-C18-C19	-172.6(2)	C31-C32-C33-C34	-0.1(4)
O1-C18-C19-C20	172.8(2)	C32-C33-C34-C35	0.9(4)
C17-C18-C19-C20	-5.4(3)	C33-C34-C35-C36	-1.2(4)
O1-C18-C19-C23	-5.2(3)	C32-C31-C36-C35	0.0(4)
C17-C18-C19-C23	176.6(2)	C34-C35-C36-C31	0.8(4)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y+1,-z+1 #2 -x+1,-y+1,-z+1

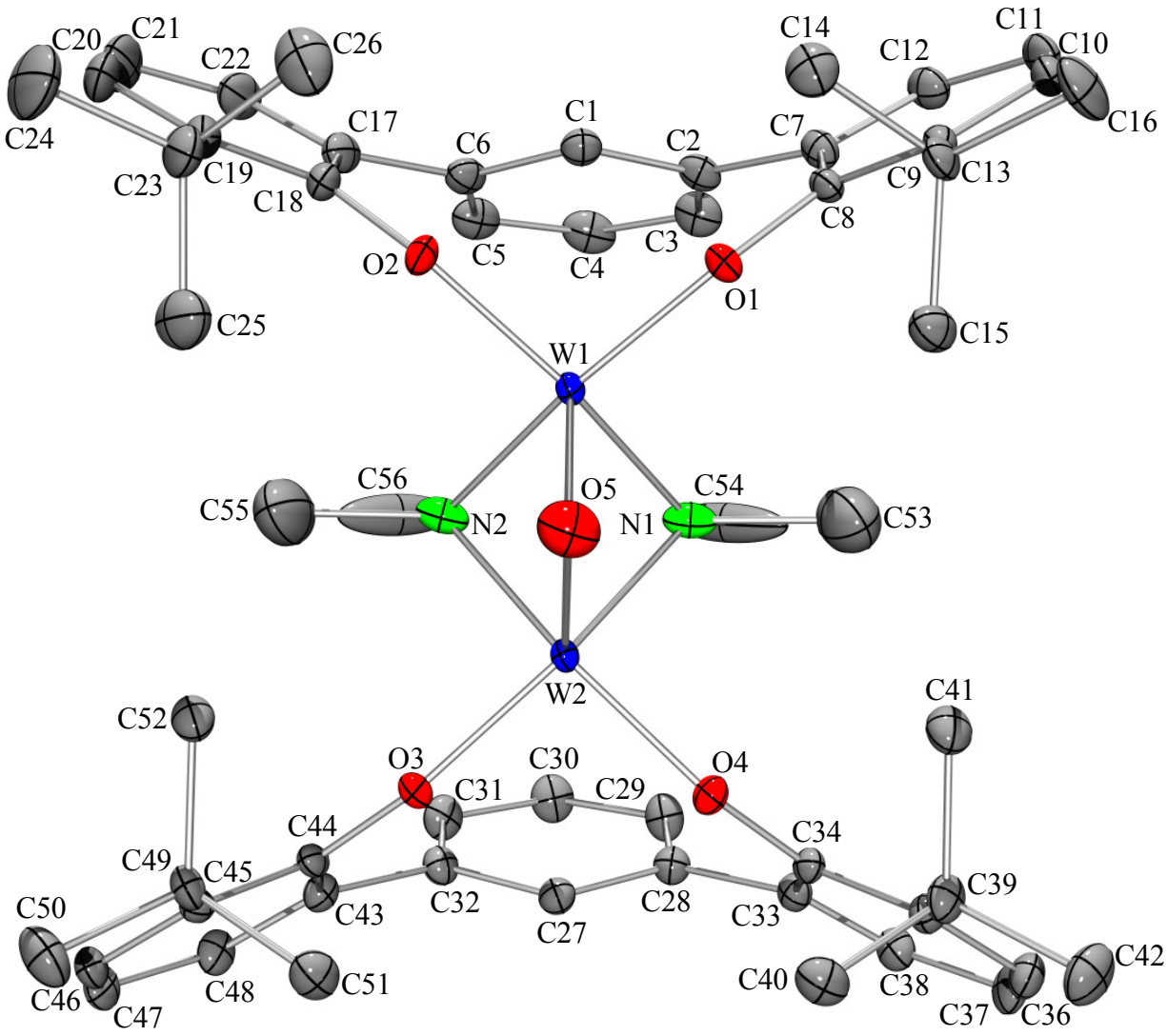


Figure B-6: Molecular structure of [^{t}BuOCHO]W(μ-NMe$_2$)$_2$(μ-O)W[^{t}BuOCHO] (**8**). Ellipsoids are shown at the 30% probability level. Hydrogens and benzene are omitted for clarity.

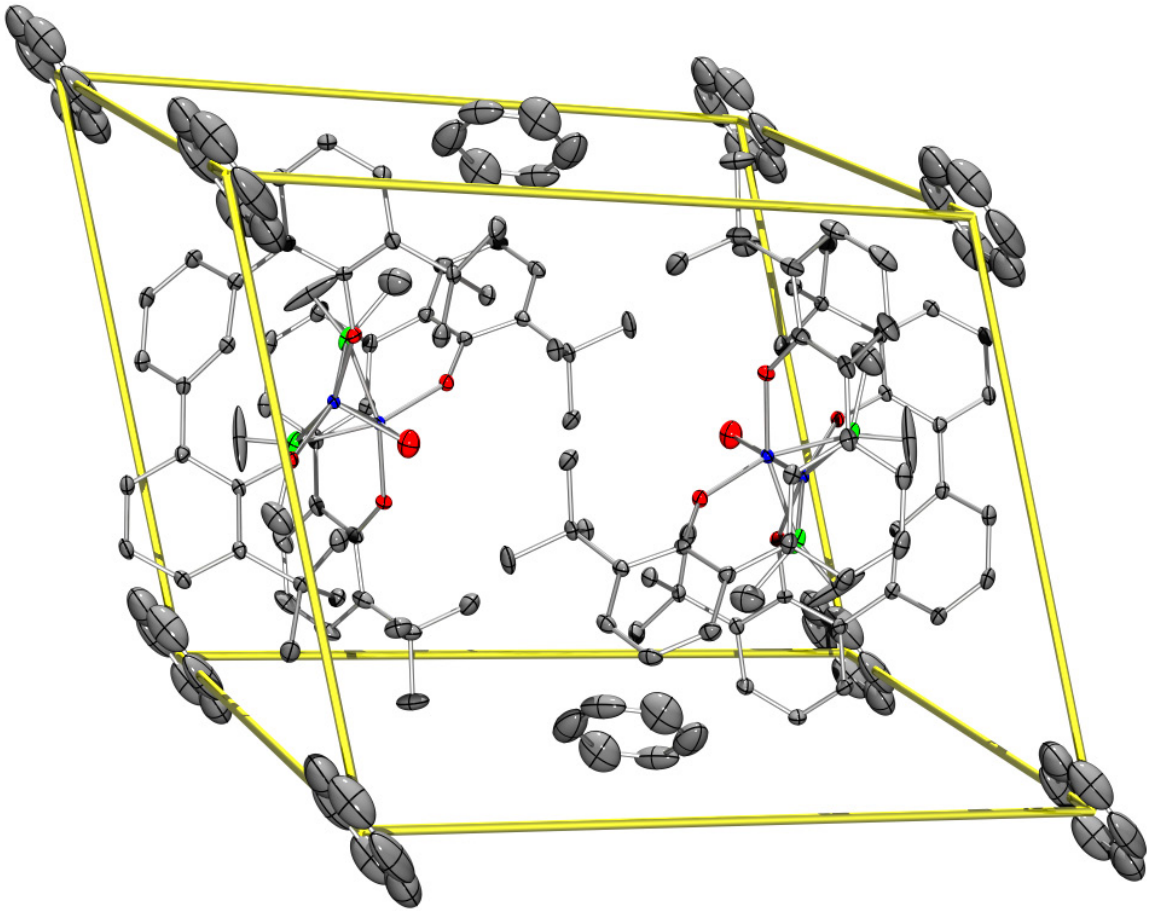


Figure B-7: Packing diagram for **8**

X-ray Experimental for [^{t}BuOCHO]W(μ-NMe$_2$)$_2$(μ-O)W[^{t}BuOCHO] (8)

Data were collected at 173 K on a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing MoKα radiation (λ = 0.71073 Å). Cell parameters were refined using up to 8192 reflections. A full sphere of data (1850 frames) was collected using the ω-scan method (0.3°frame width). The first 50 frames were re-measured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was < 1 %). Absorption corrections by integration were applied based on measured indexed crystal faces.

The structure was solved by the author using the Patterson Method in *SHELXTL6,* and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. A total of 865 parameters were refined in the final cycle of refinement using 10618 reflections (with I > 2σI) to yield R_1 and wR_2 of 2.68% and 7.24%, respectively. Refinement was done using F^2.

Table B-25: Crystal data, structure solution, and refinement for [^{t}BuOCHO]W(μ-NMe_2)$_2$(μ-O)W[^{t}BuOCHO] (**8**)

identification code	pelo9a
empirical formula	$C_{62}H_{74}N_2O_5W_2$
formula weight	1294.93
T (K)	173(2)
λ (Å)	0.71073
crystal system	Triclinic
space group	P-1
a (Å)	12.6445(7)
b (Å)	12.6890(7)
c (Å)	18.1788(10)
α (deg)	102.7360(10)
β (deg)	96.9490(10)
γ (deg)	105.3440(10)
V (Å^3)	2693.2(3)
Z	2
ρ_{calcd} (g mm^{-3})	1.597
crystal size (mm)	0.19 x 0.18 x 0.09
abs coeff (mm^{-1})	4.319
F(000)	1296
θ range for data collection	1.17 to 27.50
limiting indicies	$-16 \le h \le 16$, $-9 \le k \le 16$, $-23 \le l \le 23$
no. of reflns collcd	18368
no. of ind reflns	12501 [R(int) = 0.0372]
completeness to θ= 28.03°	97.3 %
absorption corr	Integration
refinement method	Full-matrix least-squares on F^2
data / restraints / parameters	12501 / 0 / 640
$R1$, $wR2$ [$I > 2\sigma$]	R1 = 0.0268, wR2 = 0.0724
$R1$, $wR2$ (all data)	R1 = 0.0328, wR2 = 0.0766
GOF on F^2	0.684
largest diff. peak and hole (e.Å^{-3})	2.014 and -1.299

$R1 = \Sigma(||F_o| - |F_c||) / \Sigma|F_o|$

$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

$S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$

$w = 1/[\sigma^2(F_o^2)+(m*p)^2+n*p]$, $p = [\max(F_o^2,0)+ 2* F_c^2]/3$, m & n are constants.

Table B-26: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for [^{t}BuOCHO]W(μ-NMe_2)$_2$(μ-O)W[^{t}BuOCHO] (**8**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	X	Y	Z	U(eq)
W1	2069(1)	4567(1)	3039(1)	17(1)
W2	3372(1)	5187(1)	2182(1)	16(1)
N1	2440(3)	6082(3)	2751(2)	32(1)
N2	1763(3)	4111(3)	1853(2)	32(1)
O1	2127(2)	5316(2)	4111(1)	23(1)
O2	1292(2)	3017(2)	3049(1)	24(1)
O3	4615(2)	6568(2)	2371(1)	22(1)
O4	3850(2)	4292(2)	1340(1)	20(1)
O5	3604(3)	4555(3)	3049(2)	54(1)
C1	-75(3)	4392(3)	3394(2)	26(1)
C2	27(3)	5539(3)	3603(2)	27(1)
C3	-577(3)	5963(4)	3097(2)	35(1)
C4	-1208(3)	5245(4)	2412(2)	39(1)
C5	-1230(3)	4128(4)	2184(2)	36(1)
C6	-654(3)	3671(3)	2675(2)	29(1)
C7	736(3)	6236(3)	4347(2)	26(1)
C8	1743(3)	6024(3)	4600(2)	22(1)
C9	2347(3)	6534(3)	5355(2)	23(1)
C10	1977(3)	7352(3)	5812(2)	30(1)
C11	1048(4)	7650(3)	5548(2)	34(1)
C12	421(3)	7076(3)	4831(2)	32(1)
C13	3327(3)	6151(3)	5674(2)	26(1)
C14	2918(4)	4891(4)	5622(2)	37(1)
C15	4292(3)	6386(4)	5239(2)	33(1)
C16	3794(4)	6771(4)	6524(2)	45(1)
C17	-652(3)	2481(3)	2495(2)	31(1)

Table B-26: Continued

Atom	X	Y	Z	U(eq)
C18	306(3)	2191(3)	2747(2)	27(1)
C19	267(4)	1048(3)	2687(2)	35(1)
C20	-743(4)	226(4)	2293(3)	47(1)
C21	-1651(4)	500(4)	1988(3)	54(1)
C22	-1626(4)	1616(4)	2106(3)	44(1)
C23	1265(4)	735(3)	3047(3)	41(1)
C24	982(6)	-559(4)	2939(4)	70(2)
C25	2266(4)	1072(4)	2666(3)	51(1)
C26	1568(5)	1302(4)	3913(3)	54(1)
C27	3676(3)	6153(3)	831(2)	24(1)
C28	3492(3)	7179(3)	1155(2)	25(1)
C29	2507(3)	7360(3)	852(2)	31(1)
C30	1735(3)	6522(3)	258(2)	34(1)
C31	1897(3)	5479(3)	-13(2)	31(1)
C32	2880(3)	5275(3)	284(2)	25(1)
C33	4367(3)	8023(3)	1782(2)	24(1)
C34	4951(3)	7658(3)	2340(2)	20(1)
C35	5912(3)	8422(3)	2871(2)	25(1)
C36	6181(3)	9552(3)	2850(2)	31(1)
C37	5560(3)	9934(3)	2339(2)	32(1)
C38	4665(3)	9167(3)	1804(2)	29(1)
C39	6627(3)	8028(3)	3435(2)	28(1)
C40	7062(3)	7099(4)	2994(2)	34(1)
C41	5947(4)	7580(3)	4006(2)	33(1)
C42	7665(4)	9002(4)	3902(3)	42(1)
C43	3141(3)	4195(3)	34(2)	24(1)
C44	3682(3)	3776(3)	588(2)	20(1)

Table B-26: Continued

Atom	X	Y	Z	U(eq)
C45	4076(3)	2831(3)	348(2)	21(1)
C46	3810(3)	2274(3)	-432(2)	26(1)
C47	3212(3)	2627(3)	-974(2)	31(1)
C48	2907(3)	3601(3)	-736(2)	29(1)
C49	4786(3)	2447(3)	929(2)	24(1)
C50	5164(4)	1452(4)	525(2)	41(1)
C51	5839(3)	3435(3)	1331(2)	33(1)
C52	4111(3)	2060(3)	1514(2)	29(1)
C53	3079(7)	7221(6)	3451(5)	87(2)
C54	1829(8)	6733(7)	2506(6)	138(5)
C55	1603(7)	2773(6)	1432(4)	91(2)
C56	916(5)	3985(10)	1284(3)	134(5)
C57	5546(11)	598(7)	4548(7)	106(4)
C58	4417(12)	-40(10)	4308(6)	122(4)
C59	3918(10)	-627(10)	4785(8)	126(4)
C60	-162(17)	797(10)	9677(6)	135(4)
C61	812(12)	682(13)	9769(8)	131(5)
C62	1025(8)	-92(15)	10080(8)	138(5)

Table B-27: Bond lengths (in Å) for [^{t}BuOCHO]W(μ-NMe$_2$)$_2$(μ-O)W[^{t}BuOCHO] (**8**)

Bond	Length	Bond	Length
W1-O5	1.942(4)	C6-C17	1.473(6)
W1-O1	1.955(2)	C7-C12	1.403(5)
W1-O2	1.958(2)	C7-C8	1.414(5)
W1-N1	2.053(3)	C8-C9	1.407(5)
W1-N2	2.065(3)	C9-C10	1.398(5)
W1-W2	2.49726(19)	C9-C13	1.541(5)
W2-O5	1.946(3)	C10-C11	1.390(6)
W2-O3	1.951(2)	C11-C12	1.372(6)
W2-O4	1.954(2)	C13-C14	1.523(5)
W2-N1	2.057(3)	C13-C15	1.531(5)
W2-N2	2.058(3)	C13-C16	1.534(5)
N1-C54	1.377(7)	C17-C22	1.398(5)
N1-C53	1.639(8)	C17-C18	1.411(6)
N2-C56	1.345(6)	C18-C19	1.417(5)
N2-C55	1.649(8)	C19-C20	1.406(6)
O1-C8	1.347(4)	C19-C23	1.535(7)
O2-C18	1.357(4)	C20-C21	1.375(8)
O3-C34	1.351(4)	C21-C22	1.375(7)
O4-C44	1.343(4)	C23-C25	1.524(7)
C1-C2	1.387(5)	C23-C26	1.533(7)
C1-C6	1.403(5)	C23-C24	1.546(6)
C2-C3	1.408(5)	C27-C32	1.386(5)
C2-C7	1.475(5)	C27-C28	1.396(5)
C3-C4	1.376(6)	C28-C29	1.397(5)
C4-C5	1.379(6)	C28-C33	1.484(5)
C5-C6	1.399(5)	C29-C30	1.393(5)
C30-C31	1.385(6)	C58-C59	1.368(14)
C31-C32	1.404(5)	C59-C57#1	1.303(15)

Table B-27: Continued

Bond	Length	Bond	Length
C32-C43	1.482(5)	C60-C61	1.274(17)
C33-C38	1.390(5)	C60-C62#2	1.401(16)
C33-C34	1.412(5)	C61-C62	1.305(18)
C34-C35	1.424(5)	C62-C60#2	1.401(16)
C35-C36	1.395(5)		
C35-C39	1.535(5)		
C36-C37	1.393(5)		
C37-C38	1.380(5)		
C39-C41	1.535(5)		
C39-C40	1.540(5)		
C39-C42	1.543(5)		
C43-C48	1.391(5)		
C43-C44	1.423(5)		
C44-C45	1.420(5)		
C45-C46	1.392(5)		
C45-C49	1.545(5)		
C46-C47	1.392(5)		
C47-C48	1.386(6)		
C49-C52	1.526(5)		
C49-C51	1.535(5)		
C49-C50	1.535(5)		
C55-C56	2.006(14)		
C57-C59#1	1.303(15)		
C57-C58	1.403(15)		

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z #2 -x+1,-y+2,-z+1

Table B-28: Bond angles (in deg) for [^{t}BuOCHO]W(μ-NMe_2)$_2$(μ-O)W[^{t}BuOCHO] (**8**)

Bond	Angle	Bond	Angle
O5-W1-O1	101.84(13)	O3-W2-W1	129.66(7)
O5-W1-O2	103.16(13)	O4-W2-W1	130.19(7)
O1-W1-O2	98.21(10)	N1-W2-W1	52.51(9)
O5-W1-N1	90.02(14)	N2-W2-W1	52.85(9)
O1-W1-N1	91.98(12)	C54-N1-C53	85.0(6)
O2-W1-N1	161.22(12)	C54-N1-W1	135.3(4)
O5-W1-N2	89.79(14)	C53-N1-W1	116.6(3)
O1-W1-N2	163.12(11)	C54-N1-W2	130.4(4)
O2-W1-N2	90.89(12)	C53-N1-W2	119.2(3)
N1-W1-N2	75.65(14)	W1-N1-W2	74.83(12)
O5-W1-W2	50.09(10)	C56-N2-C55	83.5(6)
O1-W1-W2	127.71(7)	C56-N2-W2	132.8(4)
O2-W1-W2	127.88(7)	C55-N2-W2	117.1(3)
N1-W1-W2	52.66(9)	C56-N2-W1	136.7(4)
N2-W1-W2	52.60(9)	C55-N2-W1	116.3(3)
O5-W2-O3	106.30(13)	W2-N2-W1	74.55(12)
O5-W2-O4	105.94(13)	C8-O1-W1	146.2(2)
O3-W2-O4	96.54(10)	C18-O2-W1	140.8(2)
O5-W2-N1	89.80(14)	C34-O3-W2	147.0(2)
O3-W2-N1	90.92(12)	C44-O4-W2	148.8(2)
O4-W2-N1	159.79(11)	W1-O5-W2	79.94(13)
O5-W2-N2	89.89(14)	C2-C1-C6	123.0(3)
O3-W2-N2	159.10(11)	C1-C2-C3	117.7(4)
O4-W2-N2	91.43(12)	C1-C2-C7	118.3(3)
N1-W2-N2	75.71(14)	C3-C2-C7	123.9(4)
O5-W2-W1	49.97(10)	C4-C3-C2	119.5(4)
C3-C4-C5	122.0(4)	C20-C19-C18	116.0(4)
C4-C5-C6	120.1(4)	C20-C19-C23	122.3(4)

Table B-28: Continued

Bond	Angle	Bond	Angle
C5-C6-C1	117.2(4)	C18-C19-C23	121.6(4)
C5-C6-C17	124.3(4)	C21-C20-C19	122.7(4)
C1-C6-C17	118.5(3)	C20-C21-C22	120.3(4)
C12-C7-C8	118.5(3)	C21-C22-C17	120.2(5)
C12-C7-C2	122.0(3)	C25-C23-C26	110.8(4)
C8-C7-C2	119.4(3)	C25-C23-C19	111.2(4)
O1-C8-C9	119.5(3)	C26-C23-C19	109.6(4)
O1-C8-C7	119.5(3)	C25-C23-C24	106.3(4)
C9-C8-C7	121.1(3)	C26-C23-C24	107.5(4)
C10-C9-C8	117.0(3)	C19-C23-C24	111.3(4)
C10-C9-C13	121.9(3)	C32-C27-C28	122.9(3)
C8-C9-C13	121.0(3)	C27-C28-C29	117.8(3)
C11-C10-C9	122.5(4)	C27-C28-C33	118.2(3)
C12-C11-C10	119.3(3)	C29-C28-C33	124.0(3)
C11-C12-C7	121.0(4)	C30-C29-C28	120.0(4)
C14-C13-C15	109.6(3)	C31-C30-C29	120.9(3)
C14-C13-C16	107.1(3)	C30-C31-C32	120.0(4)
C15-C13-C16	107.4(3)	C27-C32-C31	117.9(3)
C14-C13-C9	109.5(3)	C27-C32-C43	117.6(3)
C15-C13-C9	111.9(3)	C31-C32-C43	124.5(3)
C16-C13-C9	111.2(3)	C38-C33-C34	119.3(3)
C22-C17-C18	119.0(4)	C38-C33-C28	120.7(3)
C22-C17-C6	120.1(4)	C34-C33-C28	119.9(3)
C18-C17-C6	120.9(3)	O3-C34-C33	120.3(3)
O2-C18-C17	119.8(3)	O3-C34-C35	118.7(3)
O2-C18-C19	118.9(3)	C33-C34-C35	120.9(3)
C17-C18-C19	121.4(3)	C36-C35-C34	116.5(3)

Table B-28: Continued

Bond	Angle	Bond	Angle
C36-C35-C39	121.3(3)	C52-C49-C50	107.7(3)
C34-C35-C39	122.2(3)	C51-C49-C50	107.6(3)
C37-C36-C35	122.7(4)	C52-C49-C45	110.5(3)
C38-C37-C36	119.5(3)	C51-C49-C45	108.9(3)
C37-C38-C33	120.6(3)	C50-C49-C45	111.4(3)
C41-C39-C35	110.6(3)	N2-C55-C56	41.8(3)
C41-C39-C40	109.8(3)	N2-C56-C55	54.8(5)
C35-C39-C40	110.3(3)	C59#1-C57-C58	119.6(9)
C41-C39-C42	107.8(3)	C59-C58-C57	118.3(10)
C35-C39-C42	111.7(3)	C57#1-C59-C58	122.1(11)
C40-C39-C42	106.5(3)	C61-C60-C62#2	119.8(13)
C48-C43-C44	119.1(3)	C60-C61-C62	121.4(12)
C48-C43-C32	121.3(3)	C61-C62-C60#2	118.9(12)
C44-C43-C32	119.5(3)		
O4-C44-C45	119.6(3)		
O4-C44-C43	120.2(3)		
C45-C44-C43	120.2(3)		
C46-C45-C44	117.4(3)		
C46-C45-C49	121.4(3)		
C44-C45-C49	121.2(3)		
C47-C46-C45	122.8(3)		
C48-C47-C46	118.8(3)		
C47-C48-C43	121.3(3)		
C52-C49-C51	110.7(3)		

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z #2 -x+1,-y+2,-z+1

Table B-29: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for [^{t}BuOCHO]W(μ-NMe_2)$_2$(μ-O)W[^{t}BuOCHO] (**8**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

Atom	**U^{11}**	**U^{22}**	**U^{33}**	**U^{23}**	**U^{13}**	**U^{12}**
W1	18(1)	17(1)	15(1)	3(1)	3(1)	5(1)
W2	18(1)	16(1)	14(1)	3(1)	3(1)	6(1)
N1	25(2)	49(2)	33(2)	23(2)	11(1)	17(2)
N2	30(2)	50(2)	28(2)	19(2)	13(1)	20(2)
O1	25(1)	26(1)	19(1)	5(1)	6(1)	11(1)
O2	24(1)	18(1)	26(1)	5(1)	2(1)	1(1)
O3	21(1)	20(1)	25(1)	8(1)	2(1)	6(1)
O4	22(1)	23(1)	16(1)	4(1)	5(1)	9(1)
O5	52(2)	66(2)	49(2)	19(2)	13(2)	21(2)
C1	23(2)	31(2)	27(2)	10(2)	6(1)	8(1)
C2	25(2)	36(2)	25(2)	10(2)	8(1)	16(2)
C3	34(2)	43(2)	38(2)	17(2)	8(2)	22(2)
C4	28(2)	61(3)	36(2)	21(2)	6(2)	23(2)
C5	22(2)	51(3)	31(2)	12(2)	1(2)	9(2)
C6	19(2)	35(2)	27(2)	7(2)	5(1)	3(1)
C7	31(2)	27(2)	24(2)	8(1)	8(1)	14(2)
C8	28(2)	21(2)	20(2)	6(1)	10(1)	10(1)
C9	30(2)	20(2)	19(2)	5(1)	9(1)	5(1)
C10	38(2)	25(2)	24(2)	2(1)	10(2)	5(2)
C11	46(2)	24(2)	35(2)	3(2)	20(2)	14(2)
C12	38(2)	30(2)	36(2)	10(2)	16(2)	18(2)
C13	31(2)	30(2)	15(2)	2(1)	3(1)	8(2)
C14	46(2)	37(2)	35(2)	16(2)	5(2)	18(2)
C15	30(2)	41(2)	27(2)	7(2)	5(2)	9(2)
C16	51(3)	63(3)	18(2)	-1(2)	-1(2)	24(2)
C17	29(2)	34(2)	21(2)	1(2)	3(1)	0(2)

Table B-29: Continued

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C18	30(2)	21(2)	26(2)	3(1)	8(1)	0(1)
C19	42(2)	24(2)	34(2)	2(2)	16(2)	3(2)
C20	53(3)	23(2)	53(3)	-3(2)	21(2)	-3(2)
C21	39(3)	40(3)	56(3)	-12(2)	7(2)	-11(2)
C22	27(2)	48(3)	37(2)	-5(2)	4(2)	-6(2)
C23	55(3)	23(2)	47(3)	10(2)	18(2)	11(2)
C24	92(5)	29(3)	97(5)	23(3)	29(4)	23(3)
C25	55(3)	41(3)	65(3)	19(2)	22(3)	22(2)
C26	78(4)	49(3)	43(3)	18(2)	8(3)	32(3)
C27	24(2)	24(2)	24(2)	9(1)	5(1)	8(1)
C28	26(2)	26(2)	24(2)	8(1)	3(1)	9(1)
C29	35(2)	31(2)	29(2)	8(2)	0(2)	16(2)
C30	33(2)	40(2)	30(2)	12(2)	-3(2)	16(2)
C31	28(2)	36(2)	26(2)	8(2)	-4(1)	8(2)
C32	28(2)	27(2)	19(2)	7(1)	3(1)	9(1)
C33	25(2)	22(2)	25(2)	6(1)	5(1)	8(1)
C34	21(2)	16(2)	23(2)	6(1)	6(1)	6(1)
C35	26(2)	24(2)	22(2)	5(1)	4(1)	6(1)
C36	34(2)	23(2)	30(2)	6(2)	2(2)	2(2)
C37	42(2)	19(2)	32(2)	7(2)	3(2)	7(2)
C38	36(2)	27(2)	29(2)	10(2)	7(2)	13(2)
C39	29(2)	27(2)	22(2)	6(1)	-3(1)	5(2)
C40	29(2)	46(2)	32(2)	12(2)	5(2)	17(2)
C41	43(2)	33(2)	24(2)	11(2)	6(2)	10(2)
C42	35(2)	41(2)	39(2)	13(2)	-9(2)	0(2)
C43	22(2)	23(2)	23(2)	7(1)	1(1)	5(1)
C44	20(2)	23(2)	15(1)	2(1)	4(1)	3(1)

Table B-29: Continued

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C45	21(2)	23(2)	18(2)	5(1)	5(1)	4(1)
C46	30(2)	25(2)	21(2)	1(1)	6(1)	7(2)
C47	36(2)	31(2)	17(2)	0(1)	1(1)	5(2)
C48	33(2)	30(2)	20(2)	6(1)	-3(1)	6(2)
C49	30(2)	24(2)	19(2)	2(1)	5(1)	12(1)
C50	55(3)	46(3)	30(2)	8(2)	10(2)	31(2)
C51	24(2)	41(2)	32(2)	7(2)	2(2)	12(2)
C52	39(2)	27(2)	25(2)	11(2)	8(2)	12(2)
C53	110(6)	69(4)	88(5)	20(4)	43(5)	29(4)
C54	178(8)	154(7)	242(11)	174(8)	186(9)	151(7)
C55	88(5)	89(5)	69(5)	-6(4)	24(4)	0(4)
C56	31(3)	289(13)	36(3)	67(5)	-12(2)	-39(5)
C57	166(10)	53(4)	130(9)	35(5)	102(8)	46(5)
C58	190(12)	136(9)	95(6)	42(6)	50(8)	123(9)
C59	111(8)	143(10)	125(9)	16(8)	62(7)	39(7)
C60	169(12)	115(9)	84(7)	-9(6)	4(8)	19(9)
C61	99(9)	140(11)	110(9)	-7(8)	55(8)	-20(8)
C62	59(5)	163(12)	124(10)	-68(8)	-9(6)	19(7)

Table B-30: Torsion angles (in deg) for [^{t}BuOCHO]W(μ-NMe_2)$_2$(μ-O)W[^{t}BuOCHO] (**8**)

Atoms	Angle	Atoms	Angle
O5-W1-O1-C10	-141.9(4)	C51-N1-W2-N2	87.4(7)
O2-W1-O1-C10	113.7(4)	C49-N1-W2-N2	-166.3(4)
N2-W1-O1-C10	-9.2(6)	W1-N1-W2-N2	-53.64(10)
N1-W1-O1-C10	-52.1(4)	C51-N1-W2-W1	141.0(7)
W2-W1-O1-C10	-92.7(4)	C49-N1-W2-W1	-112.6(4)
O5-W1-N1-C51	-174.0(7)	O2-W1-W2-O5	72.22(17)
O2-W1-N1-C51	-40.0(9)	O1-W1-W2-O5	-73.98(17)
O1-W1-N1-C51	82.8(7)	N2-W1-W2-O5	130.15(19)
N2-W1-N1-C51	-83.9(7)	N1-W1-W2-O5	-129.12(19)
W2-W1-N1-C51	-137.6(7)	O5-W1-W2-O4	-77.50(17)
O5-W1-N1-C49	76.8(4)	O2-W1-W2-O4	-5.28(12)
O2-W1-N1-C49	-149.3(5)	O1-W1-W2-O4	-151.47(13)
O1-W1-N1-C49	-26.4(4)	N2-W1-W2-O4	52.65(15)
N2-W1-N1-C49	166.9(4)	N1-W1-W2-O4	153.38(15)
W2-W1-N1-C49	113.2(4)	O5-W1-W2-O3	75.96(17)
O5-W1-N1-W2	-36.45(13)	O2-W1-W2-O3	148.18(13)
O2-W1-N1-W2	97.5(4)	O1-W1-W2-O3	1.99(12)
O1-W1-N1-W2	-139.60(10)	N2-W1-W2-O3	-153.88(15)
N2-W1-N1-W2	53.67(11)	N1-W1-W2-O3	-53.16(14)
C51-N1-W2-O5	177.5(7)	O5-W1-W2-N2	-130.15(19)
C49-N1-W2-O5	-76.2(4)	O2-W1-W2-N2	-57.93(15)
W1-N1-W2-O5	36.45(13)	O1-W1-W2-N2	155.87(15)
C51-N1-W2-O4	35.7(8)	N1-W1-W2-N2	100.72(17)
C49-N1-W2-O4	142.0(4)	O5-W1-W2-N1	129.12(19)
W1-N1-W2-O4	-105.3(3)	O2-W1-W2-N1	-158.66(15)
C51-N1-W2-O3	-76.7(7)	O1-W1-W2-N1	55.15(15)
C49-N1-W2-O3	29.7(4)	N2-W1-W2-N1	-100.72(17)
W1-N1-W2-O3	142.29(9)	O5-W1-O2-C3	144.5(4)

Table B-30: Continued

Atoms	Angle	Atoms	Angle
O1-W1-O2-C3	-110.1(4)	O2-W1-N2-W2	137.85(10)
N2-W1-O2-C3	54.0(4)	O1-W1-N2-W2	-98.5(3)
N1-W1-O2-C3	11.9(7)	N1-W1-N2-W2	-53.77(11)
W2-W1-O2-C3	96.3(4)	C9-C2-O3-W2	-152.9(3)
O5-W2-N2-C52	-171.9(6)	C5-C2-O3-W2	28.8(6)
O4-W2-N2-C52	81.7(6)	O5-W2-O3-C2	140.1(4)
O3-W2-N2-C52	-30.3(8)	O4-W2-O3-C2	-110.7(4)
N1-W2-N2-C52	-82.0(6)	N2-W2-O3-C2	0.3(6)
W1-W2-N2-C52	-136.0(6)	N1-W2-O3-C2	49.8(4)
O5-W2-N2-C50	76.7(4)	W1-W2-O3-C2	89.5(4)
O4-W2-N2-C50	-29.8(4)	W1-O2-C3-C14	-161.2(3)
O3-W2-N2-C50	-141.7(4)	W1-O2-C3-C16	19.6(6)
N1-W2-N2-C50	166.5(4)	C6-C1-O4-W2	-28.8(6)
W1-W2-N2-C50	112.5(4)	C19-C1-O4-W2	152.4(3)
O5-W2-N2-W1	-35.82(13)	O5-W2-O4-C1	-139.4(4)
O4-W2-N2-W1	-142.25(10)	O3-W2-O4-C1	111.9(4)
O3-W2-N2-W1	105.8(3)	N2-W2-O4-C1	-49.1(4)
N1-W2-N2-W1	54.06(11)	N1-W2-O4-C1	0.4(6)
O5-W1-N2-C52	167.1(6)	W1-W2-O4-C1	-88.2(4)
O2-W1-N2-C52	-90.9(6)	C62#1-C60-C61-C62	1(2)
O1-W1-N2-C52	32.8(8)	O3-C2-C5-C12	-175.5(3)
N1-W1-N2-C52	77.5(6)	C9-C2-C5-C12	6.2(5)
W2-W1-N2-C52	131.3(7)	O3-C2-C5-C22	7.0(5)
O5-W1-N2-C50	-80.0(4)	C9-C2-C5-C22	-171.3(3)
O2-W1-N2-C50	22.1(4)	O4-W2-O5-W1	128.40(11)
O1-W1-N2-C50	145.7(4)	O3-W2-O5-W1	-129.59(11)
N1-W1-N2-C50	-169.5(4)	N2-W2-O5-W1	37.36(14)

Table B-30: Continued

Atoms	Angle	Atoms	Angle
W2-W1-N2-C50	-115.8(4)	N1-W2-O5-W1	-38.26(14)
O5-W1-N2-W2	35.83(13)	O2-W1-O5-W2	-129.62(11)
O1-W1-O5-W2	128.79(11)	C14-C3-C16-C21	7.9(5)
N2-W1-O5-W2	-37.33(14)	O2-C3-C16-C26	10.3(5)
N1-W1-O5-W2	38.04(14)	C14-C3-C16-C26	-168.9(3)
O4-C1-C6-C20	174.2(3)	C19-C8-C17-C20	-2.6(6)
C19-C1-C6-C20	-7.0(5)	C22-C4-C18-C38	-7.1(5)
O4-C1-C6-C18	-9.3(5)	C22-C4-C18-C6	174.8(3)
C19-C1-C6-C18	169.5(3)	C20-C6-C18-C38	-40.2(5)
C60-C61-C62-C60#1	-1(2)	C1-C6-C18-C38	143.3(4)
O3-C2-C9-C15	175.3(3)	C20-C6-C18-C4	137.8(4)
C5-C2-C9-C15	-6.4(5)	C1-C6-C18-C4	-38.7(5)
O3-C2-C9-C30	-5.7(5)	C17-C8-C19-C1	-0.8(6)
C5-C2-C9-C30	172.7(3)	C17-C8-C19-C23	179.1(4)
W1-O1-C10-C11	-23.4(6)	O4-C1-C19-C8	-175.7(3)
W1-O1-C10-C27	156.0(3)	C6-C1-C19-C8	5.5(5)
O1-C10-C11-C40	173.0(3)	O4-C1-C19-C23	4.5(5)
C27-C10-C11-C40	-6.4(6)	C6-C1-C19-C23	-174.3(3)
O1-C10-C11-C29	-11.1(6)	C8-C17-C20-C6	1.2(6)
C27-C10-C11-C29	169.6(4)	C1-C6-C20-C17	3.5(6)
C2-C5-C12-C53	-1.4(6)	C18-C6-C20-C17	-173.0(4)
C22-C5-C12-C53	176.1(4)	C3-C16-C21-C54	-2.6(6)
C54-C13-C14-C3	0.9(5)	C26-C16-C21-C54	174.3(4)
C54-C13-C14-C45	-175.6(3)	C18-C4-C22-C25	7.3(5)
O2-C3-C14-C13	173.7(3)	C18-C4-C22-C5	-174.8(3)
C16-C3-C14-C13	-7.1(5)	C12-C5-C22-C4	-136.6(4)
O2-C3-C14-C45	-9.8(5)	C2-C5-C22-C4	40.9(5)

Table B-30: Continued

Atoms	Angle	Atoms	Angle
C16-C3-C14-C45	169.4(3)	C12-C5-C22-C25	41.1(5)
C2-C9-C15-C53	1.9(5)	C2-C5-C22-C25	-141.5(4)
C30-C9-C15-C53	-177.1(3)	C8-C19-C23-C36	116.3(4)
O2-C3-C16-C21	-172.8(3)	C1-C19-C23-C36	-63.9(5)
C8-C19-C23-C33	-122.2(4)	C11-C29-C32-C34	178.2(4)
C1-C19-C23-C33	57.6(5)	C29-C32-C34-C39	4.4(6)
C8-C19-C23-C42	-4.1(5)	C22-C25-C35-C38	-3.5(6)
C1-C19-C23-C42	175.8(4)	C10-C27-C37-C44	-0.5(7)
C4-C22-C25-C35	-1.9(6)	C47-C27-C37-C44	178.3(5)
C5-C22-C25-C35	-179.6(3)	C25-C35-C38-C18	3.7(6)
C29-C7-C26-C39	6.2(6)	C4-C18-C38-C35	1.4(6)
C29-C7-C26-C16	-174.7(3)	C6-C18-C38-C35	179.4(3)
C21-C16-C26-C7	-139.0(4)	C32-C34-C39-C26	-3.6(6)
C3-C16-C26-C7	37.8(5)	C7-C26-C39-C34	-1.6(6)
C21-C16-C26-C39	40.1(6)	C16-C26-C39-C34	179.4(4)
C3-C16-C26-C39	-143.2(4)	C10-C11-C40-C44	0.8(6)
O1-C10-C27-C37	-173.2(4)	C29-C11-C40-C44	-175.2(4)
C11-C10-C27-C37	6.2(6)	C27-C37-C44-C40	-4.9(8)
O1-C10-C27-C47	8.0(6)	C11-C40-C44-C37	4.8(7)
C11-C10-C27-C47	-172.6(4)	C13-C14-C45-C41	118.5(4)
C26-C7-C29-C32	-5.5(6)	C3-C14-C45-C41	-57.8(4)
C26-C7-C29-C11	176.3(3)	C13-C14-C45-C28	-119.9(4)
C40-C11-C29-C7	139.5(4)	C3-C14-C45-C28	63.8(4)
C10-C11-C29-C7	-36.5(5)	C13-C14-C45-C55	0.4(5)
C40-C11-C29-C32	-38.6(6)	C3-C14-C45-C55	-175.9(3)
C10-C11-C29-C32	145.4(4)	C37-C27-C47-C48	116.1(5)
C15-C9-C30-C24	-117.1(4)	C10-C27-C47-C48	-65.1(5)

Table B-30: Continued

Atoms	Angle	Atoms	Angle
C2-C9-C30-C24	63.8(4)		
C15-C9-C30-C31	120.7(4)		
C2-C9-C30-C31	-58.3(4)		
C15-C9-C30-C43	2.2(5)		
C2-C9-C30-C43	-176.8(3)		
C7-C29-C32-C34	0.1(6)		
W2-N1-C51-C49	120.7(6)		
W1-N1-C51-C49	-121.9(6)		
C5-C12-C53-C15	-3.1(6)		
C9-C15-C53-C12	2.8(6)		
C16-C21-C54-C13	-3.4(6)		
C14-C13-C54-C21	4.3(6)		
C59#2-C57-C58-C59	-0.5(16)		
C57-C58-C59-C57#2	0.6(17)		
C37-C27-C47-C46	-120.8(4)		
C10-C27-C47-C46	58.0(5)		
C37-C27-C47-C56	-1.7(6)		
C10-C27-C47-C56	177.1(4)		
W2-N1-C49-C51	-134.9(4)		
W1-N1-C49-C51	139.5(4)		

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y,-z #2 -x+1,-y+2,-z+1

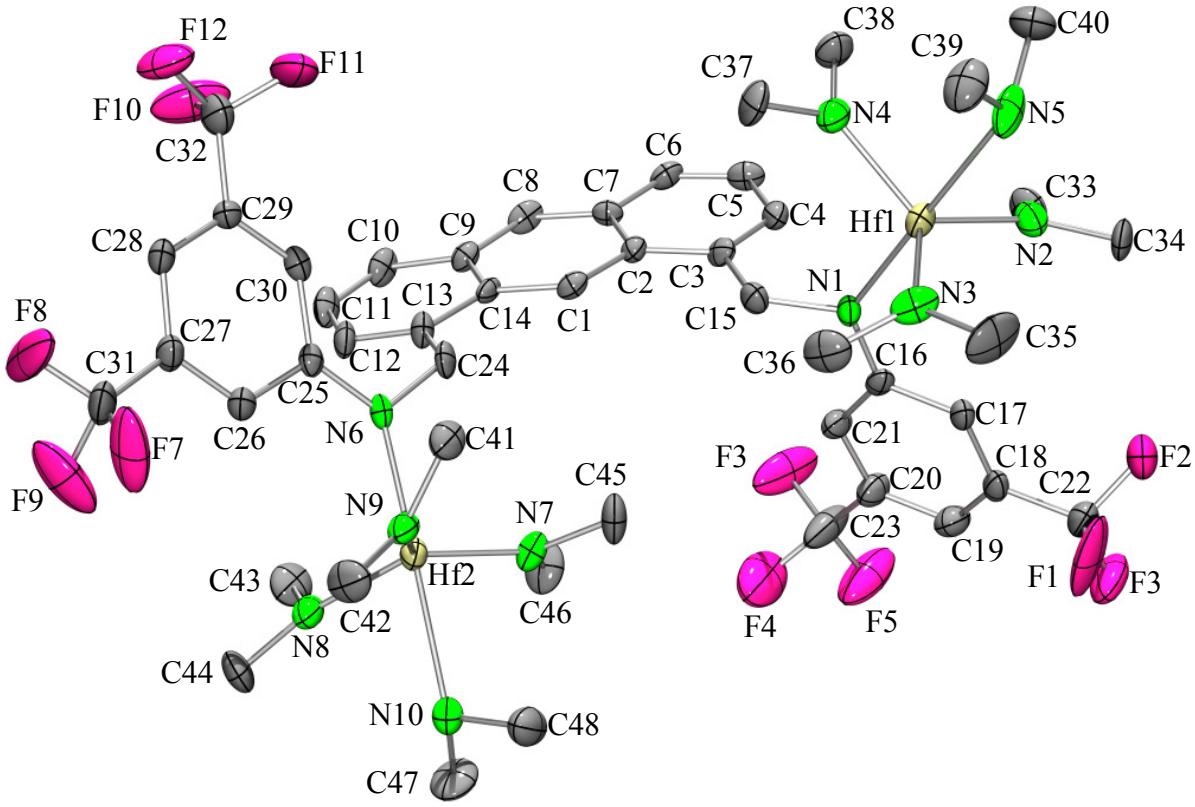


Figure B-8: Molecular structure of [AnthH][Hf(NMe$_2$)$_3$(NHMe$_2$)]$_2$ (**11**). Ellipsoids shown at 30% probability level; hydrogens omitted for clarity.

X-ray Experimental for [AnthH][Hf(NMe$_2$)$_3$(NHMe$_2$)]$_2$ (11)

Data were collected at 173 K on a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing MoKα radiation (λ = 0.71073 Å). Cell parameters were refined using up to 8192 reflections. A full sphere of data (1850 frames) was collected using the ω-scan method (0.3°frame width). The first 50 frames were re-measured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was < 1 %). Absorption corrections by integration were applied based on measured indexed crystal faces.

The structure was solved by the author using Direct Methods in *SHELXTL6,* and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. A total of 655 parameters were refined in the final cycle of refinement using 5926 reflections (with I > 2σI) to yield R_1 and wR_2 of 5.11% and 9.26%, respectively. Refinement was done using F^2.

Table B-31: Crystal data, structure solution, and refinement for $[AnthH][Hf(NMe_2)_3(NHMe_2)]_2$ (**11**)

identification code	pelo3
empirical formula	$C_{48}H_{56}F_{12}N_{10}Hf_2$
formula weight	1623.40
T (K)	173(2)
λ (Å)	0.71073
crystal system	Monoclinic
space group	P2(1)/n
a (Å)	17.3997(11)
b (Å)	20.3795(12)
c (Å)	15.9524(10)
α (deg)	90
β (deg)	93.8290
γ (deg)	90
V (Å^3)	5644.0(6)
Z	4
ρ_{calcd} (g mm^{-3})	1.598
crystal size (mm)	0.17 x 0.04 x 0.04
abs coeff (mm^{-1})	3.759
F(000)	2664
θ range for data collection	1.17 to 28.05
limiting indicies	$-22 \le h \le 16$, $-24 \le k \le 26$, $-20 \le l \le 21$
no. of reflns collcd	37974
no. of ind reflns	13605 [R(int) = 0.0990]
completeness to θ= 28.03°	99.4 %
absorption corr	Integration
refinement method	Full-matrix least-squares on F^2
data / restraints / parameters	13605 / 0 / 655
$R1$, $wR2$ [$I > 2\sigma$]	R1 = 0.0511, wR2 = 0.0926
$R1$, $wR2$ (all data)	R1 = 0.1526, wR2 = 0.1142
GOF on F^2	0.875
largest diff. peak and hole (e.Å^{-3})	1.064 and -0.893

$R1 = \Sigma(||F_o| - |F_c||) / \Sigma|F_o|$

$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

$S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$

$w = 1/[\sigma^2(F_o^2)+(m*p)^2+n*p]$, $p = [\max(F_o^2,0)+ 2* F_c^2]/3$, m & n are constants.

Table B-32: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for [AnthH][$Hf(NMe_2)_3(NHMe_2)]_2$ (**11**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	**X**	**Y**	**Z**	**U(eq)**
Hf1	1317(1)	3962(1)	3298(1)	37(1)
Hf2	6275(1)	3516(1)	1872(1)	42(1)
N1	1480(4)	4589(3)	2214(4)	36(2)
N2	162(4)	3822(3)	3001(5)	50(2)
N3	1641(4)	4658(3)	4174(4)	42(2)
N4	2084(4)	3289(3)	2962(4)	46(2)
N5	1117(4)	3277(4)	4509(5)	51(2)
N6	5265(4)	2927(3)	1471(4)	36(2)
N7	5971(4)	4295(3)	1141(5)	51(2)
N8	7068(4)	2839(3)	1498(5)	52(2)
N9	6056(5)	3572(3)	3117(4)	59(2)
N10	7444(5)	4147(4)	2266(6)	73(3)
F1	123(4)	6255(4)	4048(4)	141(3)
F2	-735(5)	5974(5)	3294(5)	150(4)
F3	-374(6)	6896(4)	3200(6)	182(5)
F4	1323(4)	7384(3)	985(4)	96(2)
F5	1054(5)	6655(3)	121(4)	136(3)
F6	2132(5)	6698(4)	737(6)	149(4)
F7	6291(5)	1010(5)	3368(4)	168(4)
F8	6216(4)	209(3)	2538(5)	126(3)
F9	6997(3)	971(3)	2390(4)	83(2)
F10	3701(5)	1115(3)	-12(5)	143(4)
F11	3218(5)	978(4)	1128(7)	152(4)
F12	3967(5)	244(3)	694(5)	145(4)
C1	3070(5)	3822(3)	449(5)	35(2)
C2	2336(4)	4021(4)	172(5)	32(2)

Table B-32: Continued

Atom	X	Y	Z	U(eq)
C3	1778(5)	4282(4)	721(5)	38(2)
C4	1053(5)	4396(4)	402(6)	45(2)
C5	836(5)	4309(4)	-467(6)	48(3)
C6	1332(5)	4110(4)	-1002(6)	46(2)
C7	2109(5)	3958(4)	-707(5)	36(2)
C8	2653(5)	3735(4)	-1243(5)	41(2)
C9	3389(5)	3532(4)	-953(5)	33(2)
C10	3931(5)	3292(4)	-1497(5)	42(2)
C11	4619(5)	3065(4)	-1207(5)	45(2)
C12	4822(5)	3060(4)	-331(6)	43(2)
C13	4331(5)	3301(4)	230(5)	38(2)
C14	3601(4)	3558(4)	-85(5)	32(2)
C15	2045(4)	4408(4)	1633(5)	40(2)
C16	1213(4)	5225(4)	2140(5)	33(2)
C17	666(5)	5463(4)	2681(5)	41(2)
C18	412(5)	6104(4)	2659(5)	43(2)
C19	656(5)	6541(4)	2079(5)	42(2)
C20	1161(5)	6316(4)	1521(5)	36(2)
C21	1421(4)	5685(4)	1534(5)	37(2)
C22	-94(7)	6327(6)	3290(8)	68(3)
C23	1393(7)	6761(5)	855(8)	65(3)
C24	4550(5)	3286(4)	1172(5)	42(2)
C25	5181(5)	2259(4)	1526(5)	37(2)
C26	5746(5)	1901(4)	2006(5)	40(2)
C27	5686(5)	1208(4)	2059(5)	44(2)
C28	5106(6)	869(5)	1639(6)	59(3)
C29	4549(6)	1221(4)	1174(6)	56(3)

Table B-32: Continued

Atom	X	Y	Z	U(eq)
C30	4573(5)	1899(4)	1124(5)	47(2)
C31	6292(6)	860(5)	2597(7)	61(3)
C32	3905(9)	884(6)	739(10)	101(5)
C33	-105(6)	3650(5)	2140(7)	69(3)
C34	-466(5)	3969(5)	3541(7)	75(3)
C35	1237(6)	4887(4)	4896(6)	63(3)
C36	2336(5)	5043(4)	4057(6)	51(3)
C37	2911(5)	3317(4)	3214(6)	59(3)
C38	1923(6)	2767(4)	2346(7)	70(3)
C39	1803(6)	3195(5)	5085(6)	69(3)
C40	756(6)	2624(4)	4272(7)	77(4)
C41	5268(7)	3737(5)	3363(6)	70(3)
C42	6596(7)	3406(5)	3849(6)	93(4)
C43	6987(5)	2497(5)	685(6)	63(3)
C44	7733(5)	2573(4)	2030(6)	64(3)
C45	5478(6)	4850(4)	1400(7)	71(3)
C46	6134(6)	4343(4)	249(6)	60(3)
C47	7899(6)	4294(5)	1491(8)	83(4)
C48	7297(6)	4751(5)	2744(7)	82(4)

Table B-33: Bond lengths (in Å) for [AnthH][Hf(NMe$_2$)$_3$(NHMe$_2$)]$_2$ (**11**)

Bond	Length	Bond	Length
Hf1-N4	2.012(7)	N10-C48	1.480(12)
Hf1-N3	2.044(7)	N10-C47	1.541(14)
Hf1-N2	2.053(7)	F1-C22	1.252(11)
Hf1-N1	2.184(7)	F2-C22	1.327(13)
Hf1-N5	2.427(8)	F3-C22	1.263(11)
Hf2-N7	2.020(7)	F4-C23	1.294(11)
Hf2-N9	2.050(7)	F5-C23	1.295(12)
Hf2-N8	2.066(7)	F6-C23	1.318(11)
Hf2-N6	2.189(6)	F7-C31	1.268(12)
Hf2-N10	2.452(8)	F8-C31	1.335(11)
N1-C16	1.379(9)	F9-C31	1.312(11)
N1-C15	1.444(10)	F10-C32	1.314(13)
N2-C33	1.463(11)	F11-C32	1.396(17)
N2-C34	1.466(12)	F12-C32	1.310(13)
N3-C36	1.463(10)	C1-C2	1.384(10)
N3-C35	1.465(11)	C1-C14	1.406(10)
N4-C38	1.462(10)	C2-C7	1.436(10)
N4-C37	1.470(10)	C2-C3	1.451(11)
N5-C39	1.467(11)	C3-C4	1.349(10)
N5-C40	1.508(11)	C3-C15	1.518(10)
N6-C25	1.373(9)	C4-C5	1.424(11)
N6-C24	1.493(9)	C5-C6	1.319(12)
N7-C46	1.473(11)	C6-C7	1.435(11)
N7-C45	1.495(11)	C7-C8	1.395(11)
N8-C43	1.471(11)	C8-C9	1.394(10)
N8-C44	1.490(10)	C9-C14	1.410(10)
N9-C42	1.488(11)	C9-C10	1.411(11)
N9-C41	1.488(12)	C10-C11	1.338(11)

Table B-33: Continued

Bond	Length	Bond	Length
C11-C12	1.418(11)		
C12-C13	1.369(11)		
C13-C14	1.432(10)		
C13-C24	1.525(10)		
C16-C21	1.412(11)		
C16-C17	1.413(11)		
C17-C18	1.379(11)		
C18-C19	1.371(11)		
C18-C22	1.454(13)		
C19-C20	1.371(11)		
C20-C21	1.364(10)		
C20-C23	1.474(13)		
C25-C30	1.406(11)		
C25-C26	1.408(10)		
C26-C27	1.418(11)		
C27-C28	1.363(11)		
C27-C31	1.493(12)		
C28-C29	1.382(11)		
C29-C30	1.385(11)		
C29-C32	1.451(14)		

Table B-34: Bond angles (in deg) for [AnthH][Hf(NMe_2)$_3$($NHMe_2$)]$_2$ (**11**)

Bond	Angle	Bond	Angle
N4-Hf1-N3	119.8(3)	C35-N3-Hf1	129.2(6)
N4-Hf1-N2	120.1(3)	C38-N4-C37	110.7(7)
N3-Hf1-N2	118.4(3)	C38-N4-Hf1	125.0(6)
N4-Hf1-N1	93.7(3)	C37-N4-Hf1	123.7(5)
N3-Hf1-N1	95.2(2)	C39-N5-C40	111.4(7)
N2-Hf1-N1	94.3(3)	C39-N5-Hf1	114.2(6)
N4-Hf1-N5	87.3(3)	C40-N5-Hf1	112.8(6)
N3-Hf1-N5	84.4(3)	C39-N5-H5	119(8)
N2-Hf1-N5	85.1(3)	C40-N5-H5	104(8)
N1-Hf1-N5	179.0(3)	Hf1-N5-H5	94(8)
N7-Hf2-N9	117.2(3)	C25-N6-C24	114.7(6)
N7-Hf2-N8	120.8(3)	C25-N6-Hf2	127.7(5)
N9-Hf2-N8	119.2(3)	C24-N6-Hf2	117.4(5)
N7-Hf2-N6	95.0(2)	C46-N7-C45	111.6(7)
N9-Hf2-N6	96.7(3)	C46-N7-Hf2	123.4(6)
N8-Hf2-N6	95.1(3)	C45-N7-Hf2	124.7(6)
N7-Hf2-N10	85.2(3)	C43-N8-C44	110.7(7)
N9-Hf2-N10	85.8(3)	C43-N8-Hf2	123.0(6)
N8-Hf2-N10	82.3(3)	C44-N8-Hf2	125.9(6)
N6-Hf2-N10	177.0(3)	C42-N9-C41	112.9(8)
C16-N1-C15	115.2(7)	C42-N9-Hf2	126.8(7)
C16-N1-Hf1	123.8(5)	C41-N9-Hf2	120.1(6)
C15-N1-Hf1	119.2(5)	C48-N10-C47	111.5(9)
C33-N2-C34	113.5(8)	C48-N10-Hf2	113.6(7)
C33-N2-Hf1	119.6(6)	C47-N10-Hf2	111.0(6)
C34-N2-Hf1	126.3(6)	C2-C1-C14	123.3(8)
C36-N3-C35	111.9(7)	C1-C2-C7	118.2(8)
C36-N3-Hf1	118.5(6)	C1-C2-C3	123.7(7)

Table B-34: Continued

Bond	Angle	Bond	Angle
C7-C2-C3	118.1(7)	C19-C18-C22	119.5(8)
C4-C3-C2	118.8(8)	C17-C18-C22	119.1(9)
C4-C3-C15	123.4(8)	C20-C19-C18	117.5(8)
C2-C3-C15	117.8(7)	C21-C20-C19	122.2(8)
C3-C4-C5	121.8(9)	C21-C20-C23	119.0(8)
C6-C5-C4	121.7(8)	C19-C20-C23	118.7(8)
C5-C6-C7	119.8(8)	C20-C21-C16	122.4(8)
C8-C7-C6	122.1(8)	F1-C22-F3	107.8(11)
C8-C7-C2	118.3(7)	F1-C22-F2	97.5(10)
C6-C7-C2	119.5(8)	F3-C22-F2	100.4(10)
C9-C8-C7	122.7(8)	F1-C22-C18	118.4(9)
C8-C9-C14	119.3(8)	F3-C22-C18	117.1(10)
C8-C9-C10	122.4(8)	F2-C22-C18	112.5(11)
C14-C9-C10	118.3(8)	F4-C23-F5	105.5(9)
C11-C10-C9	121.7(8)	F4-C23-F6	102.9(10)
C10-C11-C12	120.1(9)	F5-C23-F6	104.1(10)
C13-C12-C11	121.1(8)	F4-C23-C20	117.1(9)
C12-C13-C14	118.6(8)	F5-C23-C20	114.8(10)
C12-C13-C24	120.7(8)	F6-C23-C20	111.1(9)
C14-C13-C24	120.7(7)	N6-C24-C13	118.2(7)
C1-C14-C9	118.0(7)	N6-C25-C30	124.6(7)
C1-C14-C13	122.0(7)	N6-C25-C26	118.4(8)
C9-C14-C13	120.0(8)	C30-C25-C26	117.0(8)
N1-C15-C3	118.7(6)	C25-C26-C27	119.8(8)
N1-C16-C21	125.6(8)	C28-C27-C26	122.0(8)
N1-C16-C17	120.5(8)	C28-C27-C31	120.8(9)
C21-C16-C17	113.9(7)	C26-C27-C31	117.2(9)

Table B-34: Continued

Bond	Angle	Bond	Angle
C18-C17-C16	122.5(8)		
C19-C18-C17	121.3(8)		
C28-C29-C32	120.1(9)		
C30-C29-C32	118.0(9)		
C29-C30-C25	121.2(8)		
F7-C31-F9	105.3(10)		
F7-C31-F8	107.6(10)		
F9-C31-F8	104.1(9)		
F7-C31-C27	113.3(9)		
F9-C31-C27	114.1(9)		
F8-C31-C27	111.7(9)		
F12-C32-F10	109.0(12)		
F12-C32-F11	103.7(12)		
F10-C32-F11	99.8(11)		
F12-C32-C29	115.7(11)		
F10-C32-C29	114.8(11)		
F11-C32-C29	112.2(13)		
C27-C28-C29	118.0(9)		
C28-C29-C30	121.8(9)		

Table B-35: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for [AnthH][Hf(NMe$_2$)$_3$(NHMe$_2$)]$_2$ (**11**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

Atom	**U^{11}**	**U^{22}**	**U^{33}**	**U^{23}**	**U^{13}**	**U^{12}**
Hf1	33(1)	32(1)	47(1)	1(1)	1(1)	2(1)
Hf2	45(1)	39(1)	41(1)	2(1)	-5(1)	6(1)
N1	26(4)	38(4)	42(4)	-4(3)	5(3)	9(3)
N2	43(5)	40(4)	67(6)	12(4)	-1(4)	-1(4)
N3	39(5)	33(4)	52(5)	9(3)	-3(4)	-3(4)
N4	54(5)	40(4)	44(5)	0(3)	-8(4)	11(4)
N5	41(5)	51(5)	61(6)	8(4)	3(4)	6(4)
N6	29(4)	43(4)	35(4)	6(3)	4(3)	9(4)
N7	50(5)	41(4)	60(6)	6(4)	-5(4)	-4(4)
N8	44(5)	48(5)	64(6)	-1(4)	10(4)	1(4)
N9	96(7)	45(5)	37(5)	-4(4)	4(5)	-7(5)
N10	62(6)	48(5)	103(8)	-6(5)	-47(6)	4(5)
F1	116(6)	250(10)	58(5)	-20(5)	18(4)	106(6)
F2	90(6)	263(11)	104(6)	-57(7)	59(5)	-20(7)
F3	249(10)	109(6)	210(9)	92(6)	182(8)	130(7)
F4	150(7)	43(4)	98(5)	16(3)	40(5)	-10(4)
F5	239(10)	109(6)	58(5)	24(4)	-4(6)	-61(6)
F6	125(7)	117(6)	217(10)	100(6)	111(7)	36(5)
F7	180(8)	270(11)	52(5)	48(6)	1(5)	165(8)
F8	90(5)	62(4)	221(9)	57(5)	-28(5)	5(4)
F9	48(4)	92(4)	108(5)	28(4)	3(4)	17(4)
F10	191(8)	111(5)	112(6)	46(5)	-96(6)	-78(6)
F11	100(6)	122(7)	224(11)	44(7)	-61(7)	-43(6)
F12	180(8)	59(4)	183(8)	27(5)	-96(7)	-37(5)
C1	49(6)	25(4)	30(5)	0(4)	0(4)	0(4)
C2	27(5)	29(4)	38(5)	12(4)	-12(4)	-3(4)

Table B-35: Continued

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C3	31(5)	36(5)	45(6)	-8(4)	-5(4)	9(4)
C4	30(5)	35(5)	70(7)	-2(5)	-2(5)	11(4)
C5	31(6)	44(5)	67(7)	-12(5)	-17(5)	2(5)
C6	46(6)	44(6)	44(6)	-6(4)	-21(5)	2(5)
C7	44(5)	28(4)	36(5)	-1(4)	-4(4)	2(5)
C8	61(7)	33(5)	26(5)	-6(4)	-15(5)	-6(5)
C9	41(5)	33(5)	25(5)	-2(4)	6(4)	-6(4)
C10	57(6)	34(5)	32(5)	7(4)	-4(5)	-1(5)
C11	64(7)	40(5)	30(6)	-6(4)	12(5)	-8(5)
C12	36(5)	33(5)	60(7)	8(5)	7(5)	4(4)
C13	46(6)	24(4)	45(6)	1(4)	14(5)	9(4)
C14	34(5)	26(4)	36(5)	2(4)	2(4)	2(4)
C15	21(5)	46(5)	51(6)	-1(4)	-6(4)	8(4)
C16	24(5)	36(5)	38(5)	-3(4)	-4(4)	2(4)
C17	36(5)	44(5)	45(6)	8(4)	5(5)	7(5)
C18	42(6)	47(6)	41(6)	4(5)	8(4)	14(5)
C19	36(5)	42(5)	49(6)	6(5)	3(5)	11(5)
C20	34(5)	37(5)	37(5)	8(4)	5(4)	1(4)
C21	29(5)	45(5)	36(5)	-7(4)	3(4)	2(4)
C22	55(8)	81(8)	70(9)	30(7)	15(7)	36(7)
C23	58(8)	65(8)	73(9)	5(7)	23(7)	16(6)
C24	36(5)	49(5)	43(6)	3(4)	12(4)	6(4)
C25	44(6)	43(5)	27(5)	12(4)	13(4)	10(5)
C26	31(5)	43(5)	45(6)	9(4)	8(4)	10(5)
C27	37(6)	57(6)	41(6)	13(5)	11(5)	14(5)
C28	64(7)	48(6)	63(7)	16(5)	2(6)	-5(6)
C29	56(7)	51(6)	59(7)	16(5)	-14(6)	-5(5)

Table B-35: Continued

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C30	45(6)	44(6)	52(6)	16(5)	-6(5)	-4(5)
C31	55(8)	62(8)	66(8)	22(6)	7(6)	15(6)
C32	109(12)	61(9)	123(13)	41(8)	-62(11)	-26(9)
C33	54(7)	69(7)	81(8)	-7(6)	-16(6)	-22(6)
C34	33(6)	85(8)	109(9)	16(7)	26(6)	8(6)
C35	87(8)	56(6)	50(7)	-10(5)	29(6)	10(6)
C36	44(6)	47(5)	60(7)	1(5)	-12(5)	-8(5)
C37	42(6)	72(7)	62(7)	-9(5)	-7(5)	27(5)
C38	83(8)	46(6)	80(8)	-34(6)	-8(6)	9(6)
C39	49(7)	87(8)	69(8)	28(6)	-6(6)	-6(6)
C40	91(9)	27(5)	111(10)	5(6)	-6(7)	-21(6)
C41	96(9)	61(7)	55(7)	-11(5)	32(6)	5(6)
C42	131(11)	99(9)	43(7)	22(6)	-40(7)	-6(8)
C43	57(7)	73(7)	59(7)	-14(6)	21(6)	6(6)
C44	33(6)	61(6)	94(8)	24(6)	-16(6)	15(5)
C45	67(8)	44(6)	102(9)	9(6)	6(7)	28(6)
C46	71(7)	66(7)	43(6)	18(5)	4(6)	6(6)
C47	71(8)	83(8)	98(10)	32(7)	23(7)	-14(7)
C48	95(9)	43(6)	104(10)	-16(6)	-18(7)	4(6)

Table B-36: Torsion angles (in deg) for [AnthH][Hf(NMe_2)$_3$($NHMe_2$)]$_2$ (**11**)

Atoms	Angle	Atoms	Angle
N4-Hf1-N1-C16	-167.1(6)	N1-Hf1-N4-C37	88.7(7)
N3-Hf1-N1-C16	-46.7(6)	N5-Hf1-N4-C37	-91.4(7)
N2-Hf1-N1-C16	72.4(6)	N4-Hf1-N5-C39	62.7(7)
N4-Hf1-N1-C15	-2.8(6)	N3-Hf1-N5-C39	-57.6(7)
N3-Hf1-N1-C15	117.7(5)	N2-Hf1-N5-C39	-176.8(7)
N2-Hf1-N1-C15	-123.3(6)	N4-Hf1-N5-C40	-65.8(6)
N4-Hf1-N2-C33	-49.7(7)	N3-Hf1-N5-C40	173.9(7)
N3-Hf1-N2-C33	145.4(6)	N2-Hf1-N5-C40	54.7(6)
N1-Hf1-N2-C33	47.1(6)	N7-Hf2-N6-C25	159.5(7)
N5-Hf1-N2-C33	-133.7(6)	N9-Hf2-N6-C25	-82.3(7)
N4-Hf1-N2-C34	139.8(7)	N8-Hf2-N6-C25	37.9(7)
N3-Hf1-N2-C34	-25.1(8)	N7-Hf2-N6-C24	-26.6(6)
N1-Hf1-N2-C34	-123.4(7)	N9-Hf2-N6-C24	91.5(6)
N5-Hf1-N2-C34	55.8(7)	N8-Hf2-N6-C24	-148.2(5)
N4-Hf1-N3-C36	51.6(6)	N9-Hf2-N7-C46	176.2(6)
N2-Hf1-N3-C36	-143.5(5)	N8-Hf2-N7-C46	15.3(8)
N1-Hf1-N3-C36	-45.7(6)	N6-Hf2-N7-C46	-83.6(7)
N5-Hf1-N3-C36	135.2(6)	N10-Hf2-N7-C46	93.4(7)
N4-Hf1-N3-C35	-134.8(7)	N9-Hf2-N7-C45	-11.5(8)
N2-Hf1-N3-C35	30.1(8)	N8-Hf2-N7-C45	-172.4(6)
N1-Hf1-N3-C35	127.9(7)	N6-Hf2-N7-C45	88.6(7)
N5-Hf1-N3-C35	-51.2(7)	N10-Hf2-N7-C45	-94.3(7)
N3-Hf1-N4-C38	179.9(7)	N7-Hf2-N8-C43	-54.2(7)
N2-Hf1-N4-C38	15.3(8)	N9-Hf2-N8-C43	145.3(6)
N1-Hf1-N4-C38	-81.9(7)	N6-Hf2-N8-C43	44.7(7)
N5-Hf1-N4-C38	98.0(8)	N10-Hf2-N8-C43	-133.9(7)
N3-Hf1-N4-C37	-9.5(8)	N7-Hf2-N8-C44	133.4(6)
N2-Hf1-N4-C37	-174.2(6)	N9-Hf2-N8-C44	-27.1(8)

Table B-36: Continued

Atoms	Angle	Atoms	Angle
N6-Hf2-N8-C44	-127.7(7)	C1-C2-C7-C8	-3.4(11)
N10-Hf2-N8-C44	53.7(7)	C3-C2-C7-C8	177.2(7)
N7-Hf2-N9-C42	-133.0(7)	C1-C2-C7-C6	175.0(7)
N8-Hf2-N9-C42	28.2(8)	C3-C2-C7-C6	-4.3(11)
N6-Hf2-N9-C42	127.8(7)	C6-C7-C8-C9	-174.3(7)
N10-Hf2-N9-C42	-50.6(7)	C2-C7-C8-C9	4.1(12)
N7-Hf2-N9-C41	52.9(7)	C7-C8-C9-C14	-0.5(12)
N8-Hf2-N9-C41	-145.9(6)	C7-C8-C9-C10	178.4(7)
N6-Hf2-N9-C41	-46.3(7)	C8-C9-C10-C11	-176.2(7)
N10-Hf2-N9-C41	135.3(7)	C14-C9-C10-C11	2.8(12)
N7-Hf2-N10-C48	66.0(7)	C9-C10-C11-C12	0.2(12)
N9-Hf2-N10-C48	-51.7(7)	C10-C11-C12-C13	-1.8(12)
N8-Hf2-N10-C48	-172.0(8)	C11-C12-C13-C14	0.3(12)
N7-Hf2-N10-C47	-60.6(6)	C11-C12-C13-C24	179.3(7)
N9-Hf2-N10-C47	-178.3(6)	C2-C1-C14-C9	4.1(11)
N8-Hf2-N10-C47	61.4(6)	C2-C1-C14-C13	-174.1(7)
N6-Hf2-N10-C47	34(5)	C8-C9-C14-C1	-3.5(11)
C14-C1-C2-C7	-0.6(11)	C10-C9-C14-C1	177.5(7)
C14-C1-C2-C3	178.7(7)	C8-C9-C14-C13	174.8(7)
C1-C2-C3-C4	-173.1(7)	C10-C9-C14-C13	-4.2(11)
C7-C2-C3-C4	6.1(11)	C12-C13-C14-C1	-179.1(7)
C1-C2-C3-C15	6.4(12)	C24-C13-C14-C1	1.9(11)
C7-C2-C3-C15	-174.3(7)	C12-C13-C14-C9	2.7(11)
C2-C3-C4-C5	-4.3(12)	C24-C13-C14-C9	-176.3(7)
C15-C3-C4-C5	176.2(8)	C16-N1-C15-C3	-74.8(9)
C3-C4-C5-C6	0.4(13)	Hf1-N1-C15-C3	119.5(6)
C4-C5-C6-C7	1.6(13)	C4-C3-C15-N1	7.2(12)

Table B-36: Continued

Atoms	Angle	Atoms	Angle
C5-C6-C7-C8	178.9(8)	C2-C3-C15-N1	-172.4(7)
C5-C6-C7-C2	0.5(12)	C15-N1-C16-C21	2.8(11)
Hf1-N1-C16-C21	167.7(6)	C12-C13-C24-N6	-7.7(11)
C15-N1-C16-C17	-179.2(7)	C14-C13-C24-N6	171.3(7)
Hf1-N1-C16-C17	-14.3(10)	C24-N6-C25-C30	17.9(11)
N1-C16-C17-C18	176.6(7)	Hf2-N6-C25-C30	-168.1(6)
C21-C16-C17-C18	-5.2(11)	C24-N6-C25-C26	-163.1(7)
C16-C17-C18-C19	2.9(13)	Hf2-N6-C25-C26	10.9(11)
C16-C17-C18-C22	-174.1(9)	N6-C25-C26-C27	-178.5(7)
C17-C18-C19-C20	0.0(13)	C30-C25-C26-C27	0.6(12)
C22-C18-C19-C20	177.0(9)	C25-C26-C27-C28	1.9(14)
C18-C19-C20-C21	-0.3(13)	C25-C26-C27-C31	-178.4(8)
C18-C19-C20-C23	176.0(9)	C26-C27-C28-C29	-2.4(14)
C19-C20-C21-C16	-2.5(13)	C31-C27-C28-C29	177.9(9)
C23-C20-C21-C16	-178.7(8)	C27-C28-C29-C30	0.5(15)
N1-C16-C21-C20	-176.9(7)	C27-C28-C29-C32	-177.9(12)
C17-C16-C21-C20	5.0(11)	C28-C29-C30-C25	2.0(15)
C19-C18-C22-F1	-122.1(12)	C32-C29-C30-C25	-179.6(11)
C17-C18-C22-F1	55.0(16)	N6-C25-C30-C29	176.6(9)
C19-C18-C22-F3	9.7(17)	C26-C25-C30-C29	-2.4(13)
C17-C18-C22-F3	-173.2(11)	C28-C27-C31-F7	-116.3(12)
C19-C18-C22-F2	125.2(10)	C26-C27-C31-F7	64.0(13)
C17-C18-C22-F2	-57.7(13)	C28-C27-C31-F9	123.2(10)
C21-C20-C23-F4	-161.4(9)	C26-C27-C31-F9	-56.5(13)
C19-C20-C23-F4	22.2(14)	C28-C27-C31-F8	5.4(14)
C21-C20-C23-F5	74.1(12)	C26-C27-C31-F8	-174.3(9)
C19-C20-C23-F5	-102.3(11)	C28-C29-C32-F12	-12(2)

Table B-36: Continued

Atoms	Angle	Atoms	Angle
C21-C20-C23-F6	-43.6(14)		
C19-C20-C23-F6	140.0(10)		
C25-N6-C24-C13	-80.3(9)		
Hf2-N6-C24-C13	105.1(7)		
C30-C29-C32-F12	169.8(12)		
C28-C29-C32-F10	-140.1(12)		
C30-C29-C32-F10	41.5(19)		
C28-C29-C32-F11	106.9(12)		

LIST OF REFERENCES

(1) Schrock, R. R. *Chem. Rev*. **2002**, *102*, 145.

(2) Schrock, R. R.; Czekelius, C. *Adv. Synth. Catal*. **2007**, *349*, 55.

(3) Schrock, R. R. *Acc. Chem. Res*. **1986**, *19*, 342.

(4) Schrock, R. R. *Angew. Chem. Int. Ed*. **2006**, *45*, 3748.

(5) North, M. in *Comprehensive Organic Functional Group Transformations II*, Katritzky, A. R.; Taylor, R. J. K., Eds. Elservier: Amsterdam, The Netherlands, **2005**; Vol 3, 621.

(6) Tyrrell, E. In *Comprehensive Organic Functional Group Transformations II*; Katritzky, A. R.; Taylor, R. J. K., Eds. Elservier: Amsterdam, The Netherlands, **2005**; Vol 1, 1083.

(7) McLain, S. J.; Wood, C.D.; Messerle, L. W.; Schrock, R. R.; Hollander, F. J.; Youngs, W. J.; Churchill, M. R. *J. Am. Chem. Soc*. **1978**, *100*, 5962.

(8) Morton, L. A.; Wang, R.; Yu, X.; Campana, C. F.; Guzei, I. A.; Yap, G. P. A.; Xue, Z. *Organometallics*. **2006**, *25*, 427.

(9) Tsai, Y. C.; Diaconescu P. L.; Cummins, C. C. *Organometallics* **2000**, *19*, 5260.

(10) Filippou, A. C.; Fischer, E. O. *J. Organomet. Chem*. **1990**, *382*, 143.

(11) Schrock, R. R.; Weinstock, I. A.; Horton, A. D.; Liu, A. H.; Schofield, M. H. *J. Am. Chem. Soc*. **1988**, *110*, 2686.

(12) Schrock, R. R.; Sancho, J.; Pederson, S. F. *Inorganic Syntheses* **1989**, *26*, 44.

(13) Tonzetich, Z. J.; Lam, Y. C.; Müller, P.; Schrock, R. R. *Organometallics* **2007**, *26*, 475.

(14) Listemann, M. L.; Schrock, R. R. *Organometallics* **1985**, *4*, 74.

(15) Fürstner, A.; Mathes, C.; Lehmann, C. W. *J. Am. Chem. Soc*. **1999**, *121*, 9453.

(16) Zhang, W.; Kraft, S.; Moore, J. S. *J. Am. Chem. Soc*. **2004**, *126*, 329.

(17) Geyer, A. M.; Gdula, R. L.; Wiedner, E. S.; Johnson, M. J. A. *J. Am. Chem. Soc*. **2007**, *129*, 3800.

(18) Bailey, B. C.; Fan, H.; Baum, E. W.; Huffman, J. C.; Baik, M.; Mindiola, D. J. *J. Am. Chem. Soc*. **2005**, *127*, 16016.

(19) Bailey, B. C.; Fout, A. R.; Fan, H.; Tomaszewski, J.; Huffman, J. C.; Gary, J. B.; Johnson, M. J. A.; Mindiola, D. J. *J. Am. Chem. Soc*. **2007**, *129*, 2234.

(20) Sarkar, S.; Carlson, A. R.; Veige, M. K.; Falkowski, J. M.; Abboud, K. A.; Veige, A. S. *J. Am. Chem. Soc*. **2008**, *130*, 1116.

(21) Choi, S.; Lin, Z. *Organometallics* **1999**, *18*, 5488.

(22) Clark, D. N.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 6774.

(23) Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverian, J. C.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc*. **1988**, *110*, 1423.

(24) Rhers, B.; Lucas, C.; Taoufik, M.; Herdtweck, E.; Dablemont, C.; Basset, J.; Lefebvre, F. *Comptes Rendus Chimie*. **2006**, *9*, 1169.

(25) Chisholm, M. H.; Eichhorn, B. W.; Folting, K.; Huffman, J. C.; Ontiveros, C. D.; Streib, W. E.; Van Der Sluys, W. G. *Inorganic Chemistry* **1987**, *26*, 3182.

(26) Ipaktschi, J.; Rooshenas, P.; Klotzbach, T.; Dülmer, A.; Hüseynova, E. *Organometallics* **2005**, *24*, 1351.

(27) Chisholm, M. H.; Huang, J.; Huffman, J. C. *J. Organomet. Chem*. **1997**, *528*, 221.

(28) Stichbury, J. C; Mays, M. J.; Davies, J. E.; Raithby, P. R.; Shields, G. P. *J. Chem. Soc., Dalton Trans.* **1997**, *13*, 2309.

(29) Koller, J.; Sarkar, S.; Abboud, K. A.; Veige, A. S. *Organometallics* **2007**, *26*, 5438.

BIOGRAPHICAL SKETCH

Andrew Peloquin was born on 18 April, 1985 in Worcester, Massachusetts, but soon moved to Deltona, Florida. He established himself as a dedicated student starting in his early educational career. He graduated from the United States Air Force Academy in Colorado Springs in May of 2007 with a Bachelor of Science degree in Chemistry. He was assigned as a chemist in the Air Force upon graduation and came directly to the University of Florida in the fall of 2007 under the Air Force Institute of Technology's Graduate Scholarship Program. Andrew joined Dr Adam Veige's group, researching metal complexes supported by trianionic pincer ligands, with a focus on high oxidation state, group VI alkylidynes. He graduated in August 2008 with a Master's of Science degree in Inorganic Chemistry.